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Metal Value Recovery from Metal Hydroxide Sludges: Removal of Iron and Recovery of Chromium

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METAL VALUE RECOVERY FROM METAL HYDROXIDE SLUDGES: REMOVAL OF IRON AND RECOVERY OF CHROMIUM

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the application of commercially developed hydrometallurgical processes to the recovery of metal values from complex metal finishing hydroxide sludges. Information in this report will be useful to the electroplating and waste disposal industries in general and to other industries responsible for treatment and disposal of metal bearing process solutions.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

METAL VALUE RECOVERY

FROM

METAL HYDROXIDE SLUDGES:

REMOVAL OF IRON AND RECOVERY OF CHROMIUM

ABSTRACT

The objectives of this investigation were to develop flowsheet(s) to separate and recover metal values from electroplating sludge materials; to collect bench scale experimental data to verify the feasibility of the proposed flowsheet(s); to demonstrate the effectiveness of the separability on a large scale (75-100 pounds of sludge per day); and to develop a first order economic evaluation of the proposed flowsheet(s) for a centralized treatment facility. The emphasis of the project was directed toward investigating the application of phosphate precipitation as a means of selectively separating iron and chromium from divalent cation species.

These objectives have been accomplished. Flowsheets and alternatives are discussed in the body of this report. The developed flowsheets have been verified to be feasible by laboratory test work. Selective metal value separations have been shown to be possible, e.g., iron and chromium can be separated from divalent metals such as zinc, nickel, and cadmium. Large scale test work has verified that effective separations are feasible and practical.

A first order economic evaluation has been performed and shows that an excellent return on investment is possible, e.g., 60 ± 18% based on recovered metal and metal salt values and 106 ± 32% if a credit is taken for disposal cost.

This report was submitted in fulfillment of Grant Number CR-812533-01 by Montana College of Mineral Science and Technology, Butte, Montana under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period October 1, 1985 - July 15, 1987.

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SECTION 1

INTRODUCTION

1.1. PROBLEM DEFINITION

In recent years increased emphasis has been placed on preventing the introduction of heavy metal- containing industrial wastewaters into publicly owned treatment works and the environment. Legislation has established regulatory authority for controlling the discharge of heavy metals into the environment. It also has mandated resource recovery whenever economically feasible. Many treatment and control technologies have come into existence to remove metals from these wastewaters, i.e., a sludge, concentrate, or regenerate form is created and is, in most cases, disposed of in a landfill. Metals are recoverable, but are not recovered significantly because of a lack of proven technologies.

Process wastewaters from the metal finishing and electroplating industry contain cyanides and heavy metals. These wastewaters have a detrimental effect on the environment if discharged directly. Such discharges are regulated by Federal, State, County and/or City ordinances, which may require installation of pretreatment technology. Some of the treatment technologies presently in use involve oxidation (or reduction), neutralization and precipitation to destroy cyanide and remove heavy metals as hydroxide sludges. Those sludges have traditionally been disposed of in hazardous landfill sites.

Disposal in landfills has certain inherent disadvantages:

1. Perpetual maintenance of the disposal site is required,
2. Dilution of the metal content occurs by mixing with other types of waste materials; and
3. Permanent loss of non-renewable metals.

If heavy metals are recovered from metal finishing sludges, it will alleviate or reduce the disposal problems and provide for conservation of energy and metal resources. The present study outlines a technical methodology for treating metal bearing sludges by hydrometallurgical techniques.

The treatment of hydroxide sludges for metal value recovery will produce several beneficial results: economic benefits from the metal values recovered will help offset the cost of recovery/treatment; non-renewable resource metals will be recycled for use by society; and there will be significantly less hazardous material to be disposed of in landfills.

1.2. BACKGROUND

Metal finishing hydroxide sludge materials are produced as a result of pollution control technology to remove heavy metal contaminants from spent electroplating electrolytes and rinse waters. Presently, most of these solids are disposed of in hazardous waste sites. The Environmental Protection Agency has supported several projects directed toward treatment of metal finishing hydroxide sludges for metal value recovery (1,2).

It has been demonstrated that conventional hydrometallurgical unit operations can be applied to mixed metal hydroxide sludge materials (1). Effective and selective separations of metal values from complex mixed metal solutions have been accomplished, e.g., separation of Fe, Cu, Zn, Cr, and Ni. However, two unit operations are high cost and high energy processes, i.e., removal of iron and oxidation and subsequent recovery of chromium.

The present study was initiated to investigate an alternative and potentially more cost-effective way for removing iron and recovering chromium from mixed metal solutions, i.e., bench scale test work by Dahnke (3) has shown that trivalent cations can very effectively be stripped from solutions in preference to divalent cations under conditions of low pH and room temperature by phosphate precipitation. The successful application of simple precipitation of iron and chromium from mixed metal solutions could mean elimination of the two high cost, high energy unit operations:

- iron removal by jarosite precipitation (the unit operation used in the previous (1) study to remove iron) requires near boiling temperatures and long residence times (four-six hours), whereas, phosphate precipitation can be accomplished at room temperature in thirty to sixty minutes.

- chromium recovery by oxidation to chromate with subsequent precipitation as a solid chromate and conversion to chromic acid requires that a difficult and slow oxidation be accomplished by use of chlorine gas or by an electrochemical cell, whereas phosphate precipitation strips chromium (+3) from solution and aqueous oxidation is unnecessary.

The substitution of relatively simple precipitation processes for the above more complex processes should significantly increase the cost-effectiveness of the overall metal value recovery sequence. The present study was, therefore, initiated to demonstrate that the bench scale separation results could be achieved on a larger more significant scale. This presentation is, then, a report on efforts to demonstrate selective and effective metal value recovery from several actual electroplating sludge materials.

1.3. BASIS FOR PHOSPHATE TEST WORK

1.3.1. STUDY METHODOLOGY

The experimental study was conducted in three phases. The third phase results are summarized in this report. The first phase study objectives were to develop preliminary flowsheets for the separation and recovery of metal values from mixed metal sludge materials; to perform laboratory studies to test the applicability of the preliminary flowsheets; to develop a test assembly of unit operations capable of treating 75-100 pounds of sludge per day, and to conduct preliminary test work in the test assembly to delineate conditions for successful operation and/or to note potential operational problems.

Phase I of the study was conducted by the Montana Tech Foundation, a not for profit organization, at its Minerals Research Center in Butte, Montana. The technical supervision of the project was performed by Dr. L. G. Twidwell, Montana Enviromet.

A team of extractive metallurgists was assembled as an advisory and review group to propose, discuss and select potential flowsheets for laboratory testing and development. The team included: Dr. L. G. Twidwell, Director of Montana Enviromet and Professor of Metallurgical Engineering at the Montana College of Mineral Science and Technology, whose expertise is pyrometallurgy and hydrometallurgy; Dr. D. Robinson, consultant for DREMCO Corporation, whose expertise is electrometallurgy and solvent extraction processes; Dr. T. J. O'Keefe, Professor of Metallurgical Engineering at the University of Missouri at Rolla, whose expertise is electrometallurgy; Dr. W. Opie, President for Research and Development, AMAX Corporation, whose expertise is extractive metallurgical techniques applied to secondary materials; Mr. A. Mehta, a consulant for Phoenix Metals, whose expertise is environmental concerns and waste processing technology as related to the electroplating industry; and Mr. J. Downey, a private consultant whose expertise is development of pilot scale studies.

The recommended flowsheets formulated by the advisory and review team were investigated at a bench scale level to ascertain applicability or non-applicability of potential unit operations. A flowsheet was developed that had several feasible alternative unit operations. Laboratory demonstrations were performed for each unit operation and each alternate unit operation. A test assembly was developed to treat 75-100 pounds of sludge material per day. Preliminary test work was conducted at the large scale during Phase I of the project.

The second phase objectives were to investigate potential alternate unit operations identified in Phase I; further test the assembly developed in Phase I; develop long-term continuous test data for the unit operations; and delineate potential process and materials handling problems.

Phase II of the study was conducted by the Montana College of Mineral Science and Technology at two locations; at the College laboratories in Butte, Montana, and at an industrial site in Camarillo, California. Large scale test work was performed at the industrial site in California. The studies included: leaching, solvent extraction, chromium oxidation and chromium precipitation. Continuous long-term solvent extraction test work and precipitation studies were performed at the College's laboratories in Butte.

The results of the Phase I and Phase II studies are summarized by Twidwell (1). The study period was July 1, 1983, until September 30, 1984.

The third phase objectives were: to conduct small scale test work to characterize the effect of temperature, time, phosphate content, and metal concentration on the precipitation of ferric and chromium phosphate; to conduct large scale test work (in the test assembly developed during Phase I and II of the previous studies) to demonstrate the effectiveness and selectivity of the proposed iron and chromium phosphate unit operations. Selected sludges were then treated for iron removal and chromium recovery.

The study period for the Phase III test work was October 1, 1985 through July 15, 1987. Phase III test work was conducted in the research laboratories at the Montana Colege of Mineral Science and Technology in Butte, Montana.

1.3.2. FEATURES OF THE PHOSPHATE PRECIPITATION PROCESS

Phosphate precipitation is an ideal way to remove trivalent metal ions from divalent metal ions. It has several important features that make it a preferred means of removing aqueous metal cations from a solution:

- Selectivity in acid solution is excellent for removal of trivalent cations from divalent and monovalent cations. Therefore, Fe(+3) or Al(+3) or Cr(+3) can be precipitated selectively from Zn(+2), Ni(+2), etc., bearing solutions. Also trivalent cations can be, in some cases, selectively separated from other trivalent cations.

- Solid/Liquid Separation is excellent because the precipitated phase consists of agglomerated spherites. The filterability feature is very important, i.e., the phosphate products filter easily and can be compacted to a high solids content.

- Conversion of the phosphate precipitate to a hydroxide product (and subsequently to a disposable or marketable product) regenerates the phosphorus reagent for reuse; thereby improving the process economics.

1.3.2.1. Selectivity of the Phosphate Process

Solubility diagrams for the trivalent cation phosphates: ferric, chromium and aluminum, are presented in Figures 1.1-1.3. Included on the figures are the phase boundaries for hydroxide stability. These diagrams were calculated from data (25°C) tabulations of Baes and Mesmer (4), Wagman et al. (5), Robins (6), Naumov et al. (7), Nriagu and Moore (8). Diagrams for the divalent cation phosphates; zinc, nickel, ferrous, and cadmium, are presented in Figures 1.4-1.7. Generation of solubility diagrams allow for comparisons of potential separations, e.g., iron from zinc (see notes on Figure 1.8); chromium from nickel (see notes on Figure 1.9). From such diagrams it is apparent that iron(III) or chromium(III) should be selectively precipitated from zinc or nickel in acid solutions. In general, it can be stated that trivalent cation phosphates can be stripped selectively from solutions containing divalent cations under acid conditions, i.e., divalent cation phosphates are much more soluble at low pH values than are trivalent cation phosphates.

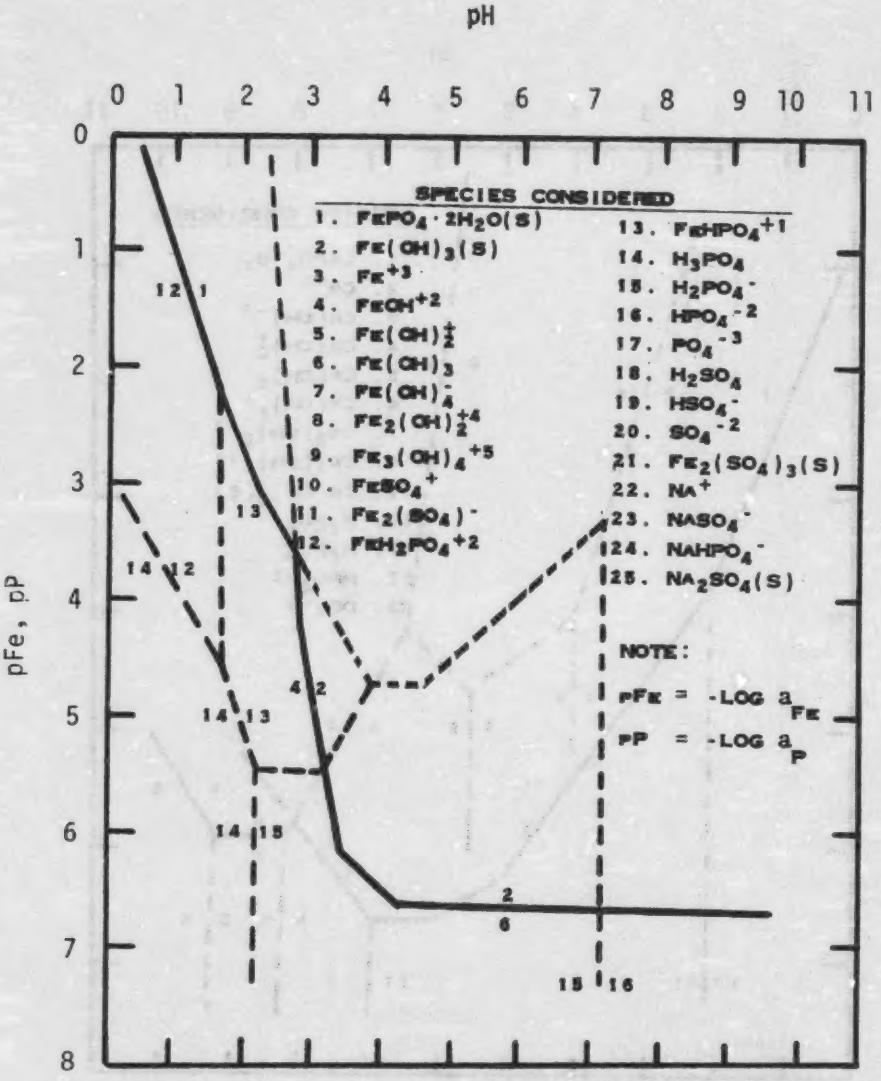

FIGURE 1.1. FERRIC PHOSPHATE STABILITY DIAGRAM FOR THE FERRIC-PHOSPHATE-SULFATE-WATER SYSTEM.

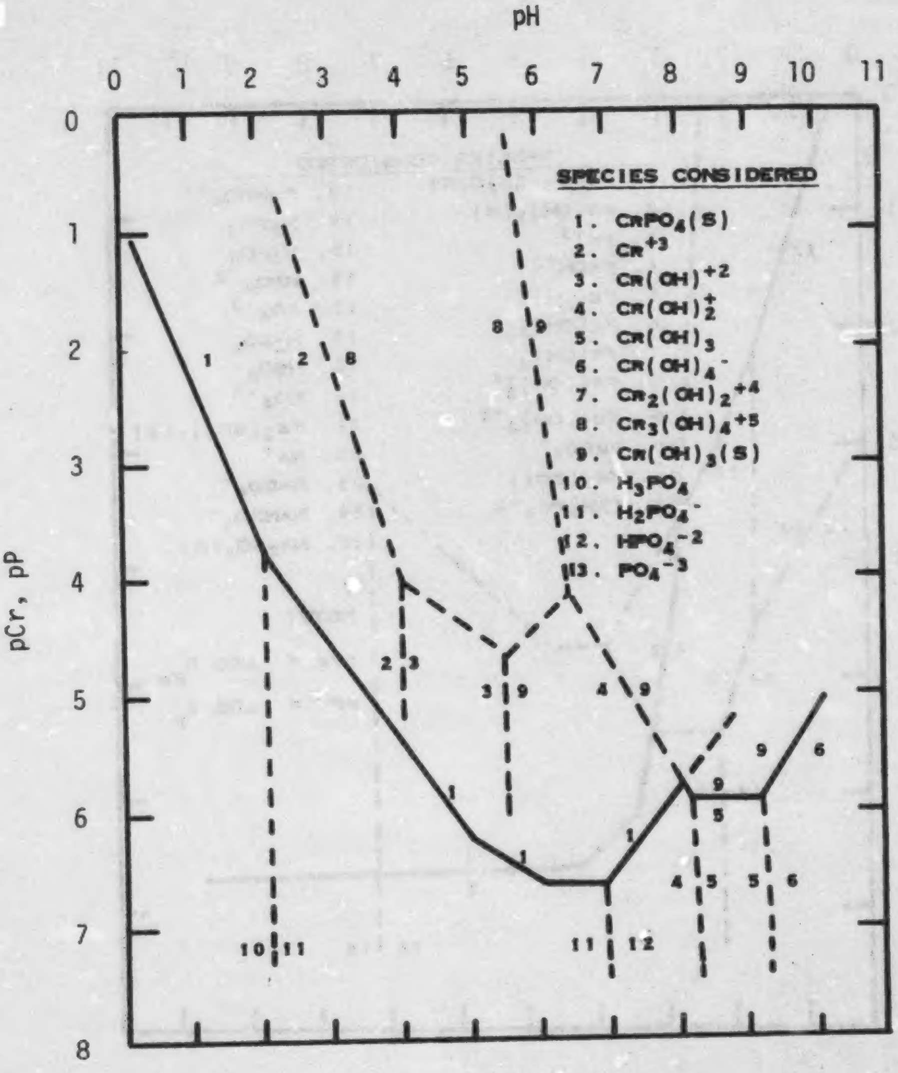

FIGURE 1.2. CHROMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CHROMIUM-PHOSPHATE-WATER SYSTEM.

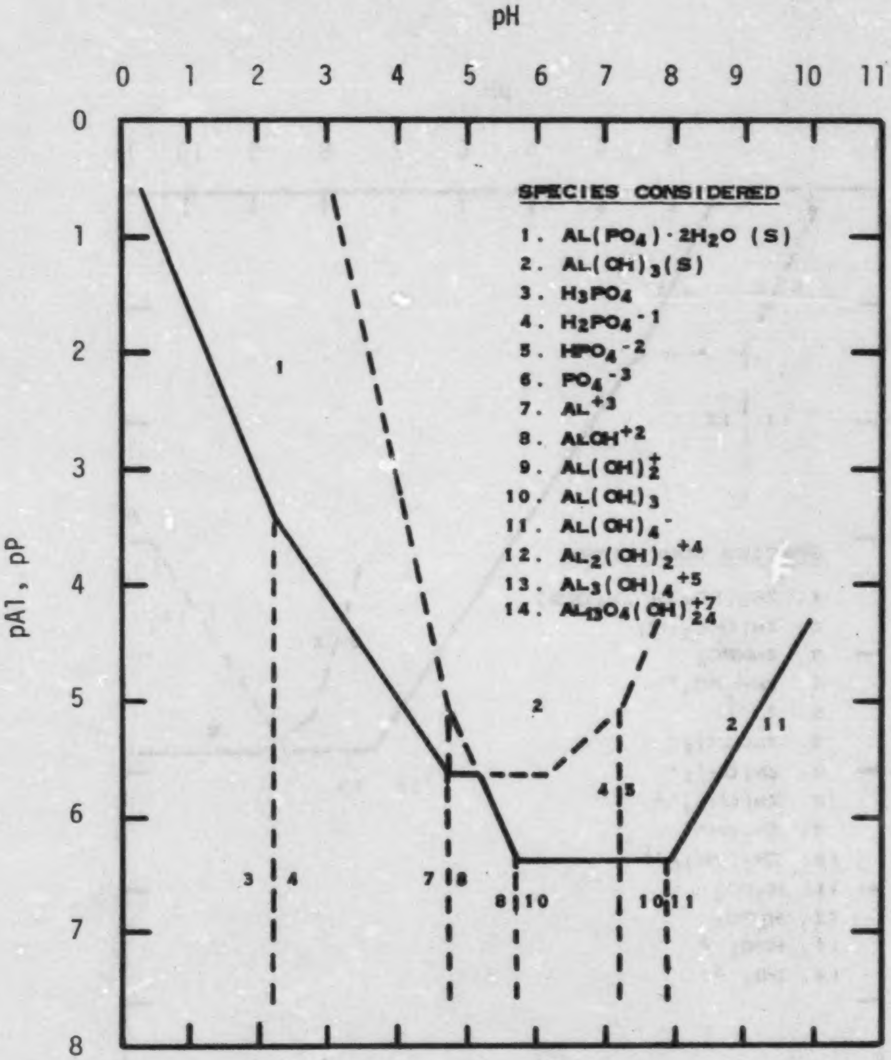

FIGURE 1.3. ALUMIMUM PHOSPHATE STABILITY DIAGRAM FOR THE ALUMIMUM-PHOSPHATE-WATER SYSTEM.

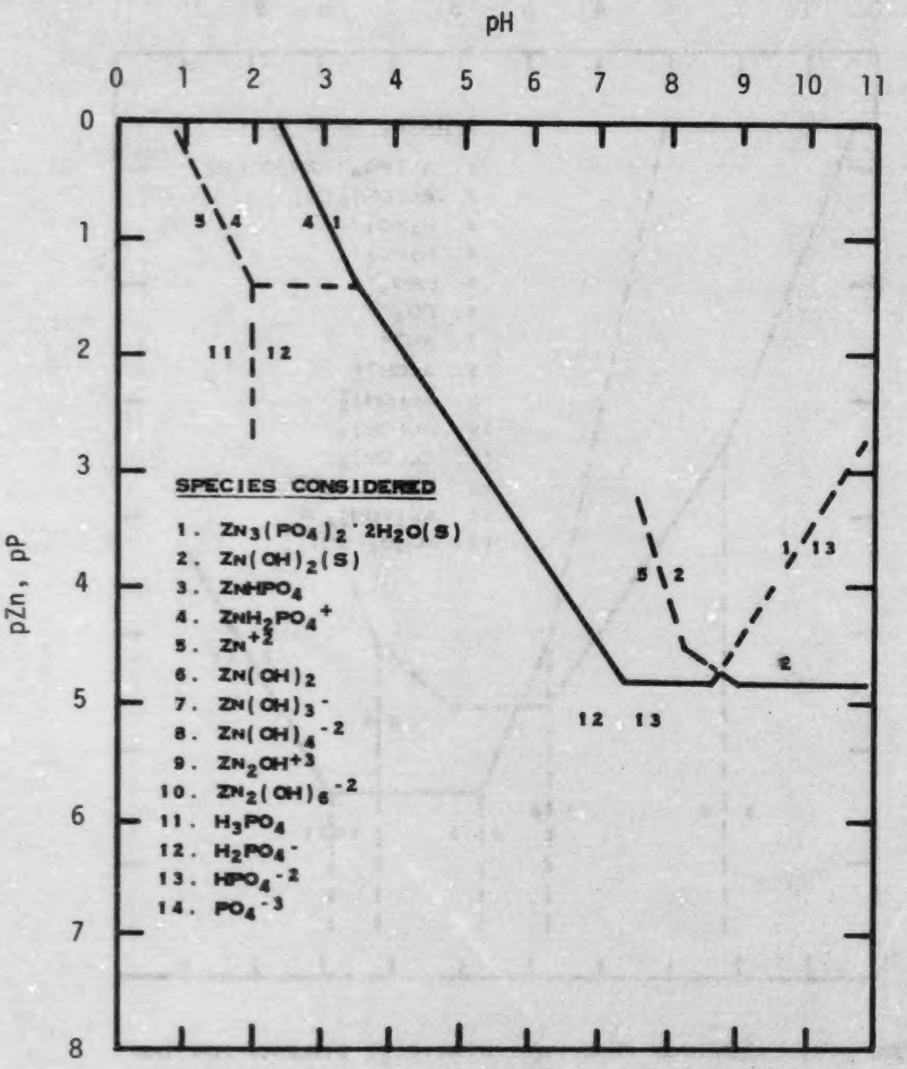

FIGURE 1.4. ZINC PHOSPHATE STABILITY DIAGRAM FOR THE ZINC-PHOSPHATE-WATER SYSTEM.

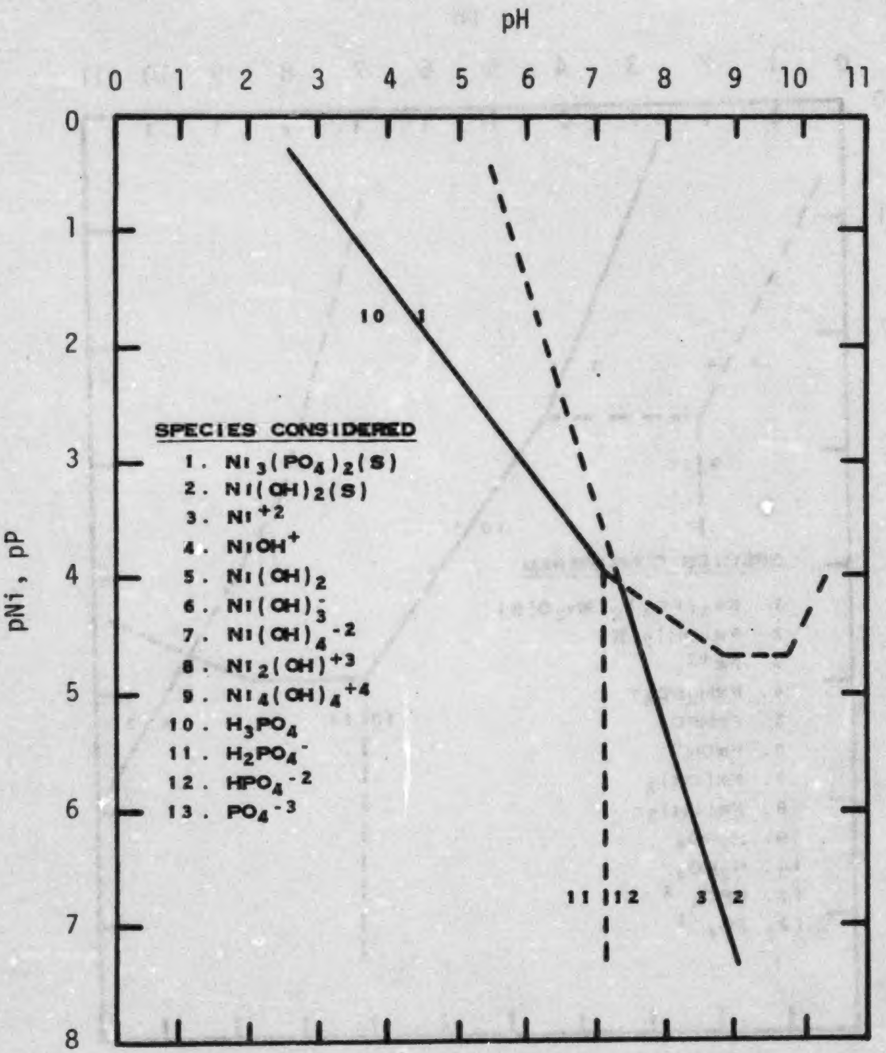

FIGURE 1.5. NICKEL PHOSPHATE STABILITY DIAGRAM FOR THE NICKEL-PHOSPHATE-WATER SYSTEM.

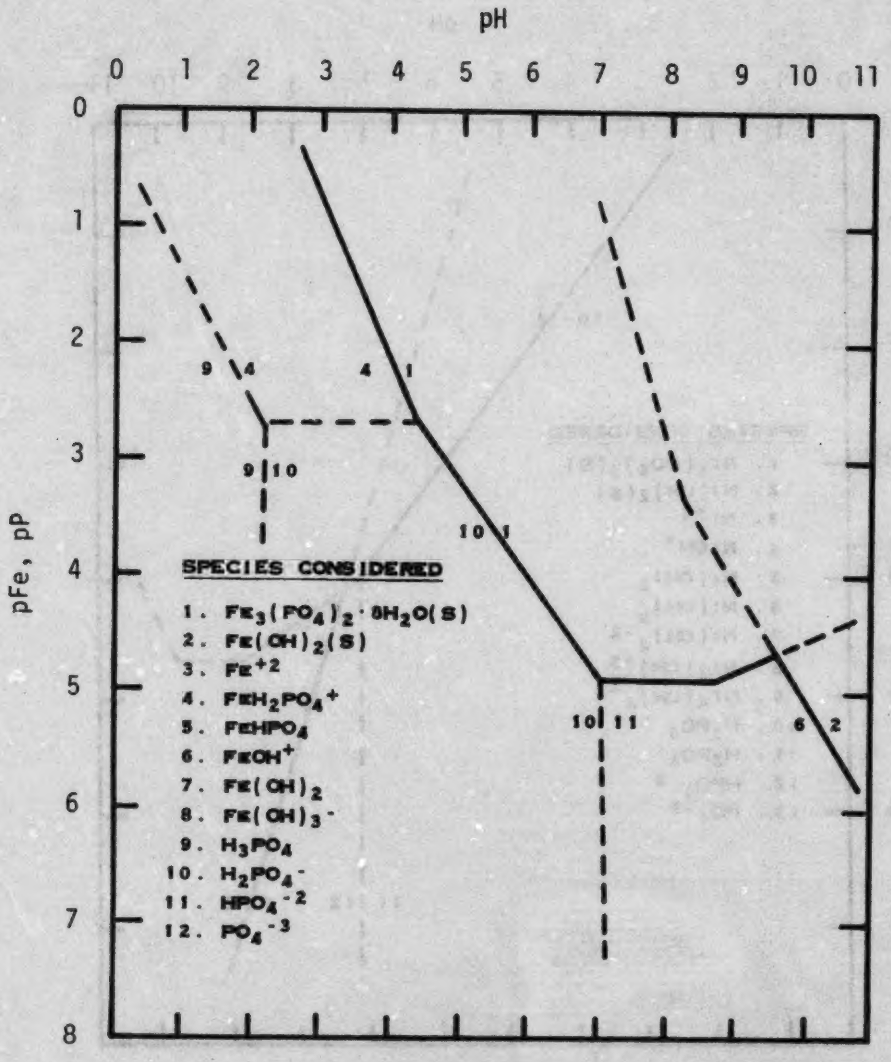

FIGURE 1.6. FERROUS PHOSPHATE STABILITY DIAGRAM FOR THE FERROUS-PHOSPHATE-WATER SYSTEM.

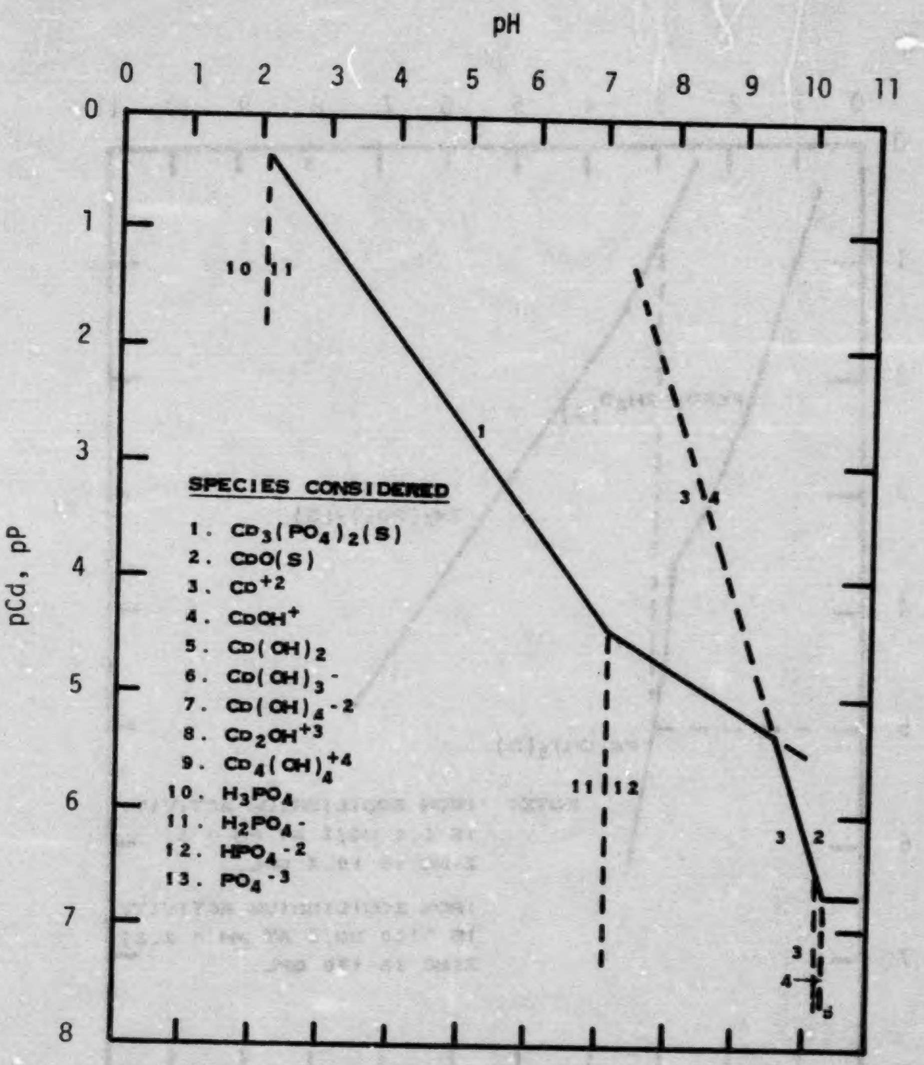

FIGURE 1.7. CADMIUM PHOSPHATE STABILITY DIAGRAM FOR THE CADMIUM-PHOSPHATE-WATER SYSTEM.

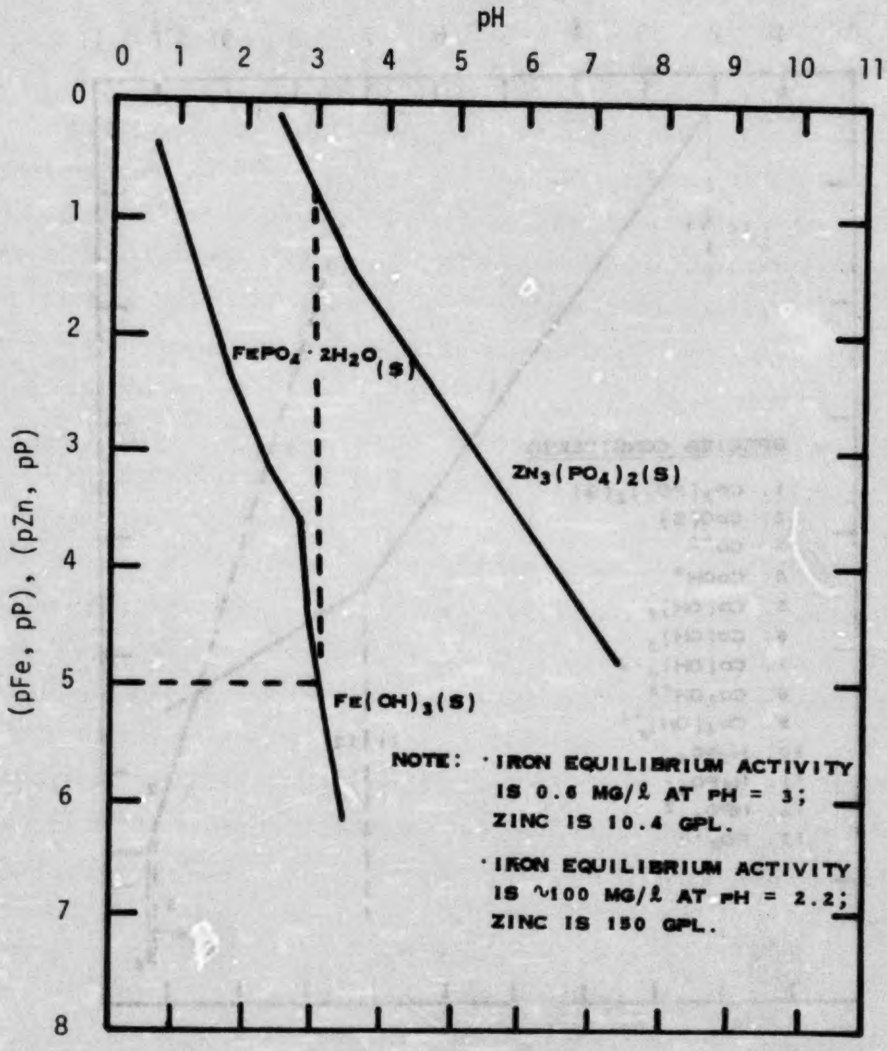

FIGURE 1.8. IRON REMOVAL FROM ZINC BY PHOSPHATE PRECIPITATION.

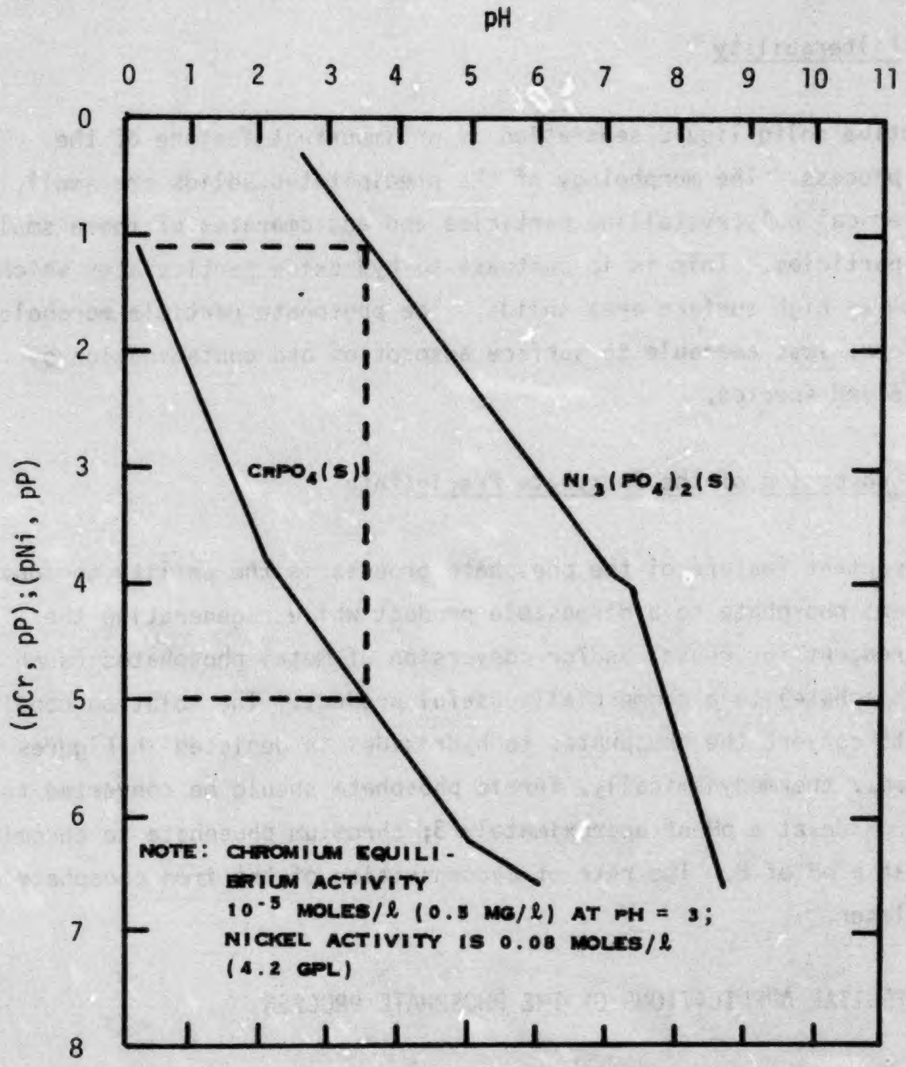

FIGURE 1.9. CHROMIUM REMOVAL FROM NICKEL BY PHOSPHATE PRECIPITATION.

Similar general statements can be made concerning the precipitation of hydroxide solids. However, hydroxide solids are difficult to filter. Whereas, phosphate precipitates are readily filterable.

1.3.2.2. Filterability

Effective solid/liquid separation is an important feature of the phosphate process. The morphology of the precipitated solids are small, dense, spherical polycrystalline particles and agglomerates of these small spherical particles. This is in contrast to hydroxide particulates which precipitate as high surface area solids. The phosphate particle morphology is, therefore, less amenable to surface adsorption and contamination by other dissolved species.

1.3.2.3. Conversion of the Phosphate Precipitate

An important feature of the phosphate process is the ability to convert the trivalent phosphate to a disposable product while regenerating the phosphate reagent for reuse; and/or conversion of metal phosphates (such as chromium phosphate) to a commercially useful product. The solution condition necessary to convert the phosphates to hydroxides is depicted in Figures 1.1-1.3, e.g., thermodynamically, ferric phosphate should be converted to ferric hydroxide at a pH of approximately 3; chromium phosphate to chromium hydroxide at a pH of 8. The rate of decomposition of the iron phosphate is discussed later.

1.3.3. POTENTIAL APPLICATIONS OF THE PHOSPHATE PROCESS

Many applications of the process are envisioned and several have been investigated at Montana Tech, e.g.,

- Removal of iron from electrolytic zinc solutions,
- Recovery of metal values from electroplating hydroxide sludge material,
- Recovery of metal values from chemical milling sludge material,

- Removal of trivalent cation impurities, Fe(+3), Al(+3) from process solutions.

1.4. PURPOSE AND OBJECTIVES OF THE PHOSPHATE PRECIPITATION STUDY

It was shown in previous experimental studies (Phase I,II) that metal values could be selectively recovered from multicomponent sludge materials. However, from an economic and energy point of view, two of the unit operations were both cost and energy intensive, i.e., removal of iron by the jarosite precipitation process and the oxidation and recovery of chromium. Therefore, application of phosphate precipitation, a process developed at Montana College of Mineral Science and Technology, was proposed for study. This process had been shown previously to allow for the selective separation of trivalent cations from divalent cations.

The specific objectives of the proposed study included:

- Small bench-scale test work to characterize the effect of temperature, time, phosphate content, and metal ion concentration on the equilibrium solubility and the rate of precipitation of ferric and chromium phosphate.

- Large scale precipitation test work (in the test assembly developed during Phases I and II of the previous study) to demonstrate the effectiveness and selectivity of the proposed iron and chromium phosphate unit operations.

SECTION 2

CONCLUSIONS

2.1. LABORATORY TEST PROGRAM

A laboratory test program has been conducted to support the development of an appropriate flowsheet made up of unit operations designed to accomplish the stated objectives of separation and metal value recovery from mixed metal hydroxide materials. The present laboratory test program was based on previous studies conducted for the Environmental Protection Agency (1,2) and on studies conducted at Montana College of Mineral Science and Technology (3). It was demonstrated in the previous studies that effective metal value separations and recoveries were possible by using industrially proven hydrometallurgical unit operations, i.e., a technology transfer was accomplished. An economic analysis of the proposed treatment sequence showed a reasonable return on investment for a large centralized treatment facility. However, two of the unit operations were energy intensive and expensive, e.g., the removal of iron by jarosite precipitation and the oxidation and subsequent recovery of chromium. Therefore, a simpler technique of metal value recovery was proposed for study.

The proposed separation technique was phosphate precipitation. Preliminary work by Dahnke (3) showed that effective and selective separations of trivalent cations from divalent cations were possible; that the precipitated solids were easily separated from solution by simple filtration devises; and that the precipitated solids were not contaminated by adsorption of divalent cations from solution.

An extremely large data base has been generated during the course of the present study. Four master of science theses have been completed that deal with some aspect of the phosphate process (3,9-11). Three additional theses are presently being prepared for publication (12-14). The results of these bench scale studies (Section 6.1.1.1 - 6.1.1.7) support the following conclusions:

- Trivalent cations can be effectively and selectively separated from divalent and monovalent solution species.

- Ferric concentrations can be lowered to a few mg/liter in acidic solutions.

- Ferric phosphate precipitation is rapid and selective over trivalent chromium and divalent cations under room temperature conditions. The precipitation kinetics and equilibrium solubility are not a strong function of temperature up to at least 50°C.

- Ferric phosphate precipitates as small spherites. Therefore, the particles show excellent filtering characteristics, i.e., they dewater rapidly during filtering and they dewater to high solids content.

- Ferric phosphate precipitates in a similar manner from acidic solutions under essentially the same experimental conditions irregardless of the solvent matrix, i.e., from sulfate, chloride, nitrate or ammonium solutions.

- Ferric phosphate can be converted to ferric hydroxide with the regeneration of the phosphate reagent by a caustic leach. The ferric hydroxide produced by the conversion process has better filtering characteristics than freshly precipitated ferric hydroxide and the converted ferric hydroxide passes the EPA:TCLP toxicity test. Therefore, it can be disposed of in a non-hazardous disposal area. Also, since the phosphate reagent can be regenerated the process economics are improved.

- Chromium phosphate precipitation is a strong function of time and temperature. Chromium phosphate requires a precipitation incubation time of several hours at room temperature but is very rapid at elevated temperatures. Therefore, the difference in the room temperature precipitation kinetics for iron and chromium provides a means for separating these two trivalent cations. Ferric phosphate can be precipitated in the presence of trivalent chromium without appreciable chromium contamination. The ferric phosphate can then be solid/liquid separated, then the chromium can be stripped by precipitation from the divalent metal species.

- Filterability of chromium phosphate precipitated from an elevated temperature solution is about the same as the filterability of ferric phosphate. Chromium phosphate also precipitates (as does ferric phosphate) as small spherites. Therefore, in addition to having good filterability, the precipitate is not contaminated by divalent cation adsorption.

- Chromium phosphate can be converted to marketable products by a soda ash roast process. High market value metal chromates or chromic acid can be produced.

Laboratory test work supports the concept that metal values can be separated and recovered effectively and efficiently from complex mixed metal sludge materials. These studies provided the basis for the subsequent large scale demonstration test work.

2.2. LARGE SCALE TEST PROGRAM

The objective of the large scale test work was to demonstrate on a significant quantity of actual sludge material that selective separations could be accomplished. The test system consisted of leach and precipitation vessels large enough to accommodate on a batch basis the treatment of up to two hundred liters of slurry, a filter press, and auxiliary pH control and monitoring instrumentation. The system is described in detail elsewhere (1). A detailed discussion of the large scale tests is presented in section 6.2.

A number of different flowsheets can be formulated to treat a given sludge material. However, a common feature of most of the flowsheets is that iron must be removed first, then chromium before any of the divalent metals. The divalent metals can also be removed by phosphate precipitation but other hydrometallurgical unit operations are available and may be used depending on the desired final product.

Large scale test work confirmed the bench scale results. Separability between metal ions and good product purity were demonstrated. Important conclusions that have resulted from the present study include:

- Sulfuric acid leaching was very effective in redissolving the metal ions from electroplating sludge. However, in the case of the electromachining sludge the leach residue contained most of the niobium and titanium and therefore provided a valuable recoverable residue.
- The weight of solids that must be disposed of, including the leach residue and converted ferric phosphate (to ferric hydroxide), was significantly less than the weight of the starting sludge, i.e., from 15-40%. Also the leach residue and ferric phosphate solids both pass the EP-TCLP test and they can, therefore, be disposed of in non-hazardous disposal sites.
- The products that are produced are of sufficient purity to serve as feedstock for commercial uses or for conversion to other more marketable products. For example, the ferric phosphate can be effectively converted to ferric hydroxide (for disposal) with the regeneration of the phosphate reagent; the high niobium - titanium leach residue should be useful as an additive in the production of microalloys; the chromium phosphate has limited marketability and must be converted to another form such as chromic acid. This conversion can be accomplished by soda ash fusion. The conversion process is also a purification process and will result in the rejection of any impurity elements like nickel and zinc.

- The filterability of the trivalent phosphates is very good. This is an important feature because it is often very difficult to dewater precipitated solids. Good filterability means the process will be more cost effective.

- Simple low cost equipment can be ultilized, i.e., simple stirred reactors, thickeners, filter presses are all that would be necessary to accomplish the separation of trivalent metals.

The large scale test work supports the concept that specific metals can be separated and recovered effectively and efficiently from complex mixed metal sludge materials.

2.3. ECONOMIC ANALYSIS

A first order economic estimate has been performed on the flowsheet presented in Figure 6.43. The calculated return on investment based on the first order estimate is normally considered to be within +30% (15,16).

Definitions and cost estimation factors are taken primarily from Mular "Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations" and Wood, Chapter 29.1, "Cost of Equipment", and Pratt, Chapter 29.2, "Cost of Process", in the "Solvent Extraction Handbook". A summary of the assumptions made and the detailed calculations for treating fifty tons of sludge per day are presented in Section 6.4 and Appendix 8.2. The major assumptions include: the land and buildings are available; and the tax rate is fifty percent of net profit. The starting sludge composition was taken to be an equal weight composite of the seven sludges used in this study; Table 6.36.

The results of the calculations are tabulated for each unit operation stage in Table 2.1. The first order estimate for the return on investment is 60 ± 18% if a credit is not taken for sludge disposal. If a credit of $125/ton is taken then the return on investment is 106 ± 32%.

A sensitivity analysis was conducted to study the influence of plant capacity on the return on investment (Tables 2.2 and 2.3). Three plant sizes were considered; 50 tons/day, 30 tons/day, and 10 tons/day. The results show a good positive return on investment for the two larger plant sizes, i.e., 60 ± 18% (50 tpd), and 38 ± 11% (30 tpd). The 10 tons/day plant size showed a return on investment of only 3 ± 1%. Detailed results of this comparison are presented in Section 6.4.2.

The detailed cost analysis results presented in Section 6.4 and 8.2 show good potential for an excellent return on investment. Even if a credit is not taken for disposal the return on investment is excellent for plant sizes greater than thirty tons per day.

TABLE 2.1. PROCESS COST: FIRST ORDER ESTIMATE

Unit Operation	Cost,$			
	F.C.C.	F.C.A.C.	Yearly Operating	Total Yearly Cost
1. Leach, S/L Separation	335,500	118,300	272,900	391,200
2. Residue Ponding	64,900	22,900	-	22,900
3. Copper SX-EW	354,000	124,800	51,200	176,000
4. Iron Precipitation, Conversion, S/L Separation	221,700	78,100	85,000	163,100
5. Chromium Precipitation, S/L Separation	102,300	36,100	199,800	235,900
6. Chromium Phosphate Fusion, Chromate Leach, Phosphate Removal, S/L Separation	253,900	89,500	1,107,700	1,197,200
7. Chromate Purification, S/L Separation, Releach, S/L Separation	201,300	71,000	29,200	100,200
8. Zinc SX, Zinc Sulfate Crystalization	436,600	153,900	61,900	215,800
9. Nickel SX-EW	265,400	93,500	38,300	131,800
	2,235,600	788,100	1,846,000	2,634,100

TABLE 2.2. PROCESS COST AS A FUNCTION OF PLANT CAPACITY

Unit Operation	Total Yearly Cost, $			Factored Capital Cost, $		
	50 TPD	30 TPD	10 TPD	50 TPD	30 TPD	10 TPD
1. Leach, S/L	391,200	287,900	148,900	335,500	246,900	127,700
2. Residue Ponding	22,900	16,900	8,700	64,900	47,800	24,700
3. Copper SX-EW	176,000	129,500	67,000	354,000	260,600	134,800
4. Iron Precipitation, Conversion, S/L	163,100	120,000	62,100	221,700	163,200	84,400
5. Chromium Precipitation, S/L	235,900	173,600	89,800	102,300	75,300	38,900
6. Chromium Phosphate Fusion, Chromate Leach, Phosphate Removal, S/L	1,197,200	881,200	455,800	253,900	186,900	96,700
7. Chromate Purification,S/L, Releach, S/L	100,200	73,700	38,100	201,300	148,200	76,600
8. Zinc SX, Zinc Sulfate Crystalization	215,800	158,800	82,200	436,600	321,300	166,200
9. Nickel SX-EW	131,800	97,000	50,200	265,400	195,300	101,000
	2,634,100	1,938,600	1,002,800	2,235,600	1,645,500	851,000

TABLE 2.3. PROCESS COST AND RETURN ON INVESTMENT AS A FUNCTION OF PLANT CAPACITY

Plant Size	F.C.C., $	Total, $/yr	R.O.I., %	
50 TPD	2,235,600	2,634,100	60 ± 18	106 ± 32*
30 TPD	1,645,500	1,938,600	38 ± 11	75 ± 23*
10 TPD	851,000	1,002,800	3 ± 1	27 ± 8*

NOTE: *Credit taken for disposal.

SECTION 3

RECOMMENDATIONS

Previous and present work have resulted in the identification of potential flowsheets that are applicable to metal value recovery from electroplating and electromachining sludge materials. Experimental studies have demonstrated on a bench scale and on an advanced larger scale that the individual unit operations are feasible. A first order economic analysis applied to the use of the phosphate process for treatment of mixed metal sludges suggests an excellent return on investment for a centralized treatment facility.

It is recommended that a pilot plant study capable of treating one ton of sludge per day be initiated. This test work is necessary to ascertain the effect of recycling process solids and final process solution back to the leach and wash operations. This study should be conducted on a composited material gathered from the area where a centralized treatment facility could be located. Therefore, pilot plant studies should be conducted and supported by the actual user of the phosphate technology.

SECTION 4

MATERIALS AND METHODS

4.1. SLUDGE CHARACTERIZATION

4.1.1. STARTING SLUDGE MATERIAL

Experimental analytical procedures and sample preparation techniques are presented in Section 5 and Appendix 8.1. For the most part, Induction Coupled Plasma Spectrophotometry (ICP) was used for determination of elemental concentrations in solutions.

Sludge materials were obtained from a variety of sources. The material was packed in fifty-five gallon barrels by the producer and shipped to Butte, Montana. The sludges were mixed metal hydroxide materials, analyses are presented in Table 4.1.

4.1.2. Methods of Analyses

Solids were digested to redissolve all the solid content. The solutions were then analyzed by ICP spectrophotometry at Montana Tech on a Perkin Elmer 5500. Solids were also semi-quantitatively analyzed by SEM-EDAX.

4.2. REAGENTS

Chemical reagents used throughout this study were either technical or reagent grade. They included: acids, bases, solid compounds such as metal sulfates, metal chlorides, etc. ASTM type II water was used for all digestions, dissolutions, and dilutions.

4.3. SOLUTION PREPARATION

Two types of solutions, synthetic and leach, were prepared for study during the course of this experimentation. The synthetic solutions usually

TABLE 4.1. MIXED METAL SLUDGE COMPOSITION AS-RECEIVED

Sludge Source	Composition in Solids, %								Solids,%
	Fe	Cr	Zn	Ni	Co	Al	Ca	Cu	
Lehr Industries (Barrel #1)	8.09	5.37	0.70	17.82	0.65	0.23	0.23	-	41.1
Lehr Industries (Barrel #2)	8.01	5.30	0.69	17.61	0.77	0.20	0.26	-	41.2
Lehr Industries (Barrel #3)	8.41	5.56	0.62	18.72	0.61	0.24	0.24	-	42.7
A.T.T. (Barrel #4)	0.62	1.00	0.97	1.41	0.13	0.18	1.72	1.55	26.7
A.T.T. (Barrel #5)	0.84	1.17	0.94	1.61	0.14	0.28	2.04	1.74	26.3
A.T.T. (Barrel #6)	0.87	1.10	0.79	1.44	0.14	0.25	1.78	1.60	25.9
N.I. Industries (Barrel #7)	2.92	8.70	10.85	-	-	1.88	1.58	-	24.7

Note: All samples were grab samples from the tops of barrels. For later test work each solid was chemically characterized before a specific test was conducted.

contained one or two heavy metals and were prepared by dissolving reagent grade salts, usually sulfates or chlorides, of the desired metals in deionized water. This type of solution was prepared to study the separation of one metal from the other without the complexities associated with the presence of other metallic species. Separation of iron from various divalent cations was studied extensively in synthetic solutions. Successful testing of a separation technique in synthetic solutions was followed by application of the technique to leach solutions produced from actual sludge material. Leach solutions were prepared to comply with a set of standard conditions which were established at Montana Tech during the course of previous work on electroplating sludges (1).

Conditions for the "standard leach" are summarized as follows:

- leach with concentrated sulfuric acid, one gram of acid per gram of solids in the sludge material.
- slurry sludge with ten percent of the desired final volume of water.
- add acid to water and leach for one hour.
- add forty percent of final volume of water to the leach.
- filter the solution and collect the wash water with the filtrate.
- dilute to 100 percent final volume, calculated to yield forty grams per liter total dissolved solids.

Several important features characterize this leaching procedure:

- Slurrying the sludge with ten percent of the final volume of water before addition of acid provides some initial dissolution of the sludge and also provides a heat sink of sufficient capacity to prevent gaseous emissions from the leach when the sulfuric acid is added.

- Temperature of the leach solution quickly rises to 50-60°C from heat of dissolution of the acid.

- Leach solution volume is one-half the process solution volume. This speeds filtration by volume reduction and allows filter cake wash water collection with the filtrate to enhance metal value recovery.

- If desired, iron can be precipitated from the undiluted leach solution. Certain impurities such as calcium, titanium, and molybdenum report with the ferric phosphate precipitate. Dilution of the filtrate from solid/liquid separation to remove ferric phosphate results in lowering the concentrations of impurities and the subsequent precipitation of cleaner salts of chromium, nickel, and cobalt.

4.4. ANALYSES

Two criteria were evaluated for the separation techniques tested: effectiveness-defined as the extent to which a particular metal could be recovered from solution, and selectivity- the purity of the precipitated metal salt. Effectiveness was determined by measuring concentrations of dissolved metals by ICP. Selectivity was also evaluated by detection of elements in solution, but more direct analysis was obtained by digesting a weighed sample of the metal salt and analyzing the resulting solution by ICP. Another technique often employed for solids analysis was SEM analysis, a method which yields semi-quantitative results for all the elements present in the salt.

SECTION 5

EXPERIMENTAL PROCEDURES

5.1. LEACH AND PRECIPITATION STUDIES

5.1.1. KETTLE TESTS

5.1.1.1. Leach Procedures

The leach and precipitation studies were conducted in one-liter thermostated reaction kettles. A typical set-up is presented in Figure 5.1. The reaction kettles allowed test work to be conducted over a wide range of experimental conditions; e.g., reaction temperature, time, acid and reagent concentrations, solution Eh, agitation rate, and solid/liquid ratio could each be varied.

The conditions for each individual experimental study were based on the particular objective for that test. As an example, an experimental leach study procedure included: selecting and blending a starting sludge sample; splitting a sample for determination of moisture content; splitting a sample for determination of elemental content; weighing the sludge sample and placing in the reaction kettle; setting the experimental temperature; initiating the study by addition of concentrated sulfuric acid; diluting the sample to the desired volume; setting the agitation rate; adjusting the pH; sampling the solution as a function of time for analysis; running the test for a designated time; removing the reaction kettle from the bath vessel; separating the solid from liquid by vacuum filtration and sampling the solution and sometimes the solid for analysis.

Each sludge was subjected to a standard sulfuric acid leach developed at Montana Tech (3,4); e.g., one-half hour; temperature 40-55°C; acid concentration equivalent to a weight of the solids content of the sludge; an initial solid/liquid ratio of 0.8; and an agitation rate to

FIGURE 5.1. LABORATORY LEACH SYSTEM

completely suspend all particles in the solution phase. The results and discussion of results are presented in Section 6.1.

5.1.1.2. Phosphate Precipitation Studies

Precipitation studies were conducted in three ways:

- The solution conditions were adjusted to conform to an experimental plan, e.g., to precipitate iron from a mixed metal solution as ferric phosphate, a predetermined amount of phosphoric acid was added. The solution temperature was stabilized and the pH was raised in increments; the pH of the solution was allowed to stabilize (20-40 minutes); a sample was withdrawn for ICP analysis and the procedure was repeated until a final desired pH was attained.

- The solution temperature and desired reagent concentration were adjusted; then the solution pH was raised immediately to a predetermined level and held constant at the desired pH for a specified time. Samples were withdrawn at periodic intervals.

- Bottle scan tests were performed. That is, when it was desirable to investigate equilibrium solubilities at different reagent concentrations or different pH values, samples were mixed and placed in polypropylene bottles and stored for short and extended times at a desired temperature. The bottle solutions were sampled periodically and analyzed for the desired constituents.

5.1.1.3. Solid/Liquid Separation

Solids were separated from the liquid by simple vacuum filtration in a Buchner filter system. If the solids were to be analyzed then several stages of precipitate washing were performed.

5.1.2. LARGE SCALE TESTS

The large-scale test work was performed in a 200-liter polypropylene reaction vessel (photographs of the large scale test assembly equipment are presented in reference 1). The experimental conditions for the large scale test work were based on the results from many kettle tests.

The experimental procedure consisted of:

- leaching the solids in a sulfuric acid solution. This was accomplished by:
    - adding enough sludge to produce a leach solution of 40 gpl dissolved metals,
    - adding sulfuric acid on the basis of one part acid/one part solid,
    - adding forty percent of the water (or recycle solution from a previous test) to provide for a final solution volume of 200 liters,
- Precipitating ferric iron or iron-chromium together or chromium in the presence of ferrous ions as metal phosphates by (usually the practice was to precipitate the ferric iron first):
    - adding sufficient phosphate to accomplish the precipitation,
    - adjusting and controlling the pH at a set value until the precipitation is complete,
    - separating the solids by filter pressing.
- Precipitating the chromium as a phosphate by:
    - adding excess phosphate to the solution,
    - raising the solution temperature to 50-80°C,
    - raising the solution pH to precipitate the chromium,
    - separating the solids by filter pressing.

- Treating the raffinate solution from the filter press for zinc or nickel recovery by a variety of means.

SECTION SIX

RESULTS AND DISCUSSION

6.1. LABORATORY TEST PROGRAM

An extremely large data base has been generated during the course of the present study. Several masters of science theses have been completed related directly to this project, e.g., Dahnke has summarized the work that produced the initial data upon which the phosphate process is based (3); Arthur investigated application of the phosphate process to chloride bearing sludge leach solutions (10); Konda investigated iron-zinc separations from high zinc solutions in a sulfate solvent matrix (9); and Nordwick studied the process of conversion of precipitated ferric phosphate to ferric hydroxide (11). These four theses are presently available in published form from Montana College of Mineral Science and Technology.

Three additional thesis presentations will soon (December 1987) be available, e.g., Rapkoch is completing a study on metal separations from ammoniated leach solutions (12); Quinn is currently experimentally investigating ways to convert chromium phosphate to marketable products (13); and McGrath is determining speciation in chromium leach solutions and the fundamental rate of precipitation of chromium phosphate (14). An additional thesis, supported by a separate funding source, is just being initiated by Donelon to study the application of the phosphate process to the recovery of metal values from stainless steel nitric-hydrofluoric acid pickling liquors (17).

Because of the problem of summarizing and representing such a large amount of data generated in the above studies, the approach used in this report is to summarize the results and conclusions of each study but to rely on the reader to solicit copies of the individual theses of interest.

Also of interest to the reader will be a number of technical professional presentations available in the open literature that resulted from the Montana

Tech study and the EPA supported study. These presentations are listed as references 18-22.

6.1.1. SUMMARY OF THESIS PROJECTS

6.1.1.1. Separation of Metal Values from Complex Metal Bearing Acidic Aqueous Sulfate Solutions

Dahnke collected the initial data which formed the foundation for the subsequent development of the phosphate process (3). Bench scale experimental work showed the following results:

6.1.1.1.1. Iron Phosphate

- Precipitated particle morphology is spherites and agglomerates of spherites. The morphology is shown in Figure 6.1. Because of the morphology, the filterability of the precipitated ferric phosphate is excellent, Table 6.1.

- Precipitation is rapid (essentially complete in 0.5 - 1 hr), Figure 6.2.

- Precipitation to less than 20 mg/liter can be accomplished from an acid solution at a pH 2.5, 25°C, without nickel or chromium coprecipitating, Figure 6.3.

- Precipitation is temperature independent up to at least 56°C, Figure 6.4.

- Precipitation is selective over divalent cations such as zinc, nickel and cadmium, Figures 6.5, 6.6.

6.1.1.1.2. Chromium Phosphate

- Precipitated particle morphology is spherites and agglomerates of spherites. The morphology is shown in Figure 6.7.

FIGURE 6.1. FERRIC PHOSPHATE PRECIPITATED FROM A MIXED METAL SOLUTION (1000X)

TABLE 6.1. FILTERABILITY OF PHOSPHATE SOLIDS

Conditions	Filterability Resistance, cm/g
$FePO_4 \cdot 2H_2O$ precipitated from 150 gpl Zn, SO_4 bearing solution, 50°C	
. pH Scan	4.01E09
. seed added	5.60E09
. product washed	4.10E09
$FePO_4 \cdot 2H_2O$ precipitated from SO_4 bearing solution, 80°C	7.30E09
$FePO4 \cdot 2H_2O$ precipitated from SO_4 bearing solution, 50°C, reslurried	4.24E09
Potassium Jarosite precipitated at pH=1.8, 90°C	7.44E09
Ferric Hydroxide precipitated at pH=3, 25°C	1.85E11

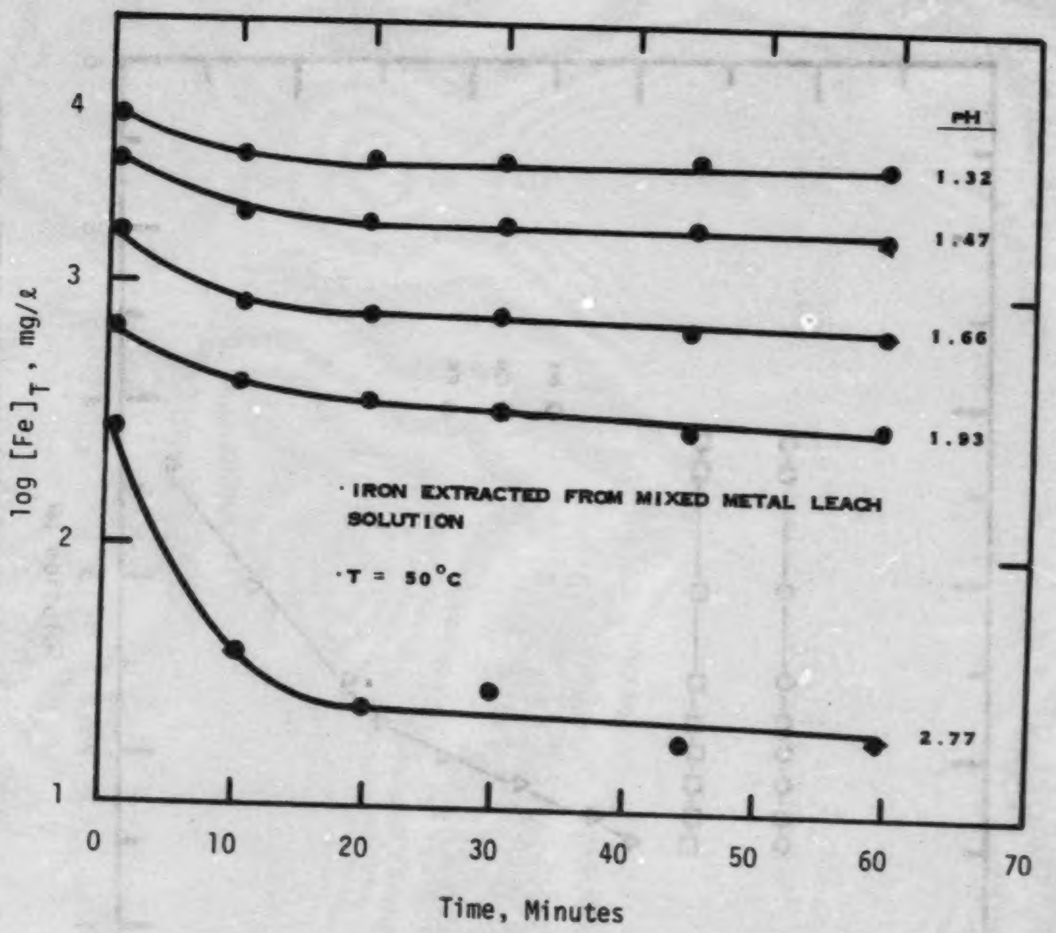

FIGURE 6.2. THE RATE OF PRECIPITATION OF FERRIC PHOSPHATE FROM A SULFATE BEARING SOLUTION

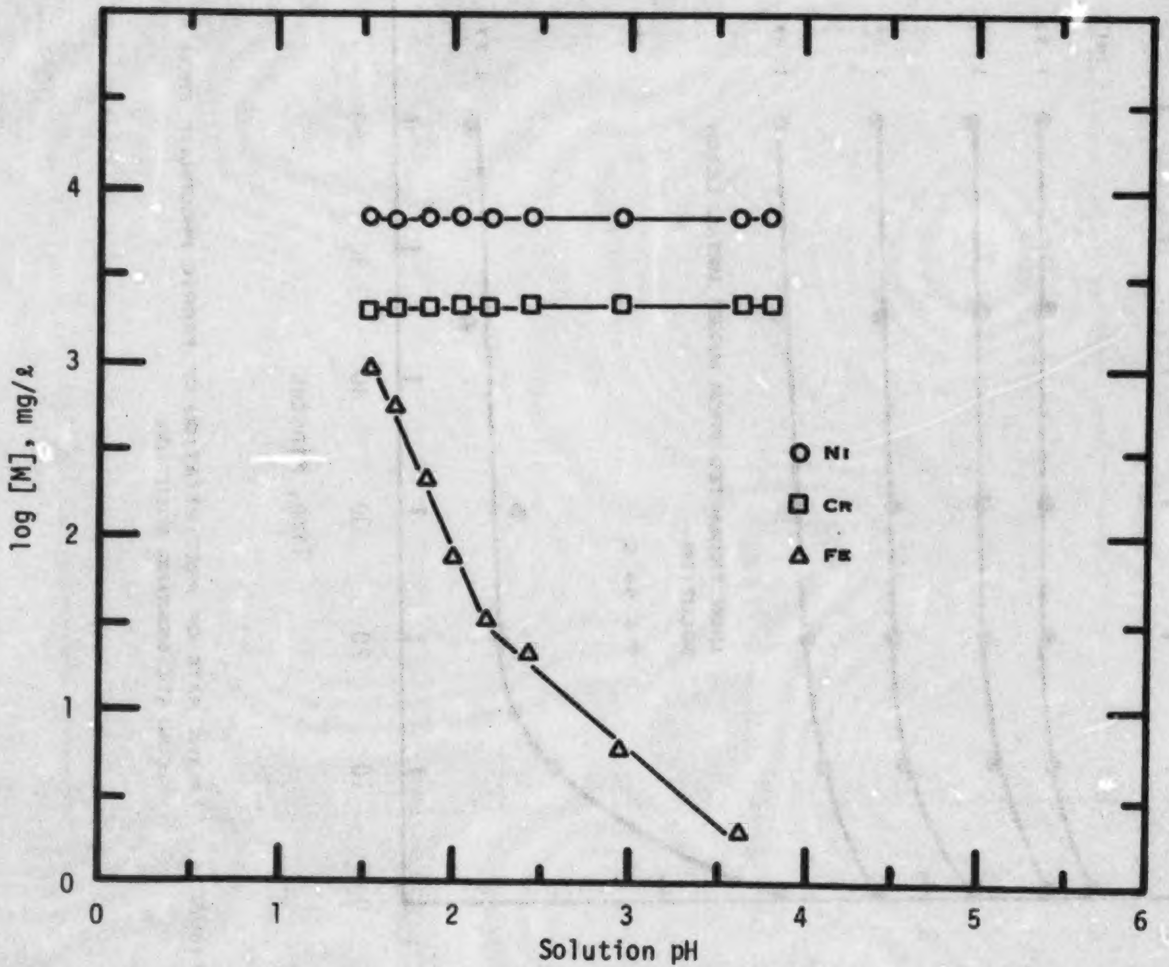

FIGURE 6.3. SELECTIVE REMOVAL OF IRON FROM CHROMIUM AND NICKEL AT ROOM TEMPERATURE

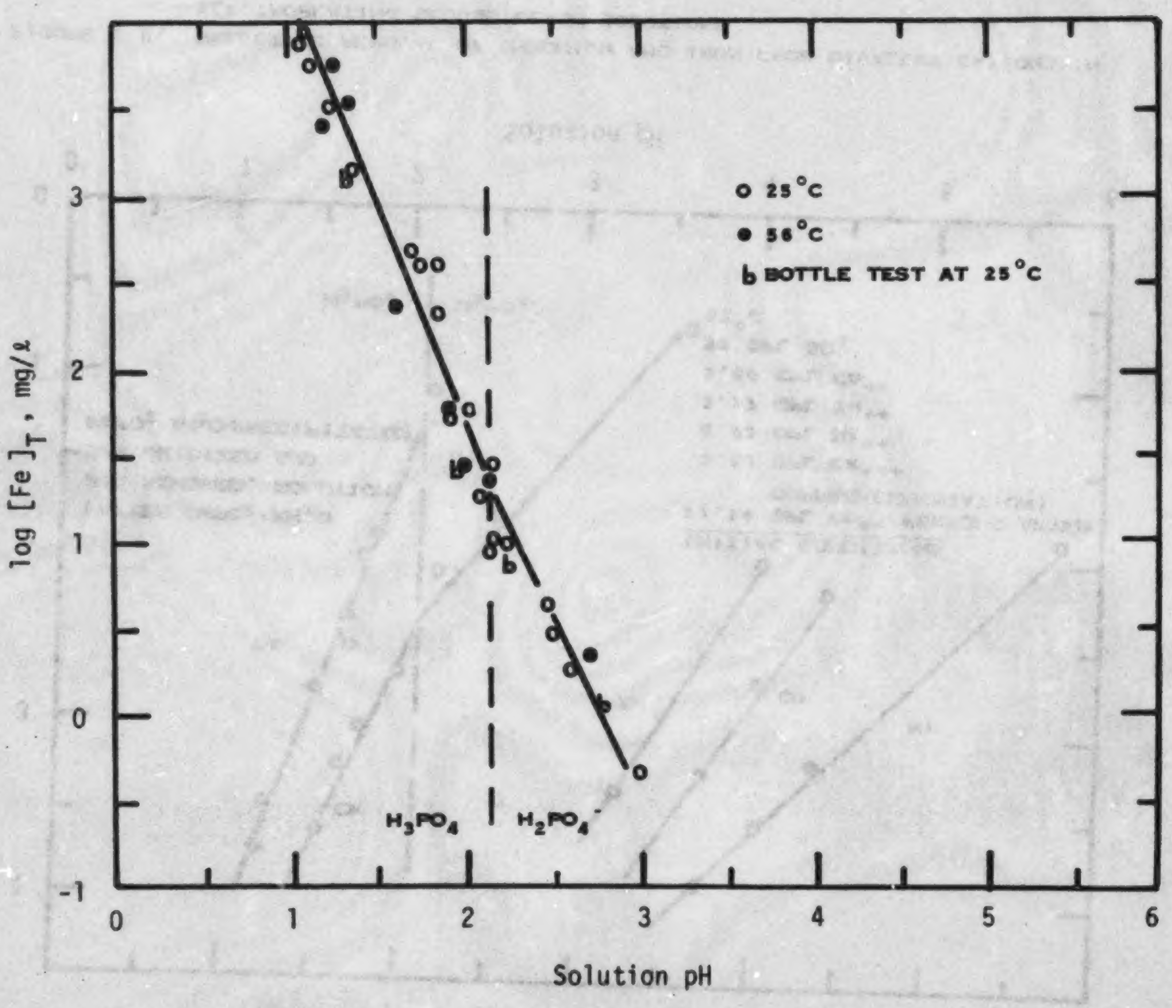

FIGURE 6.4. FERRIC PHOSPHATE PRECIPITATION FROM A CHLORIDE BEARING SOLUTION AT 25°C AND 56°C

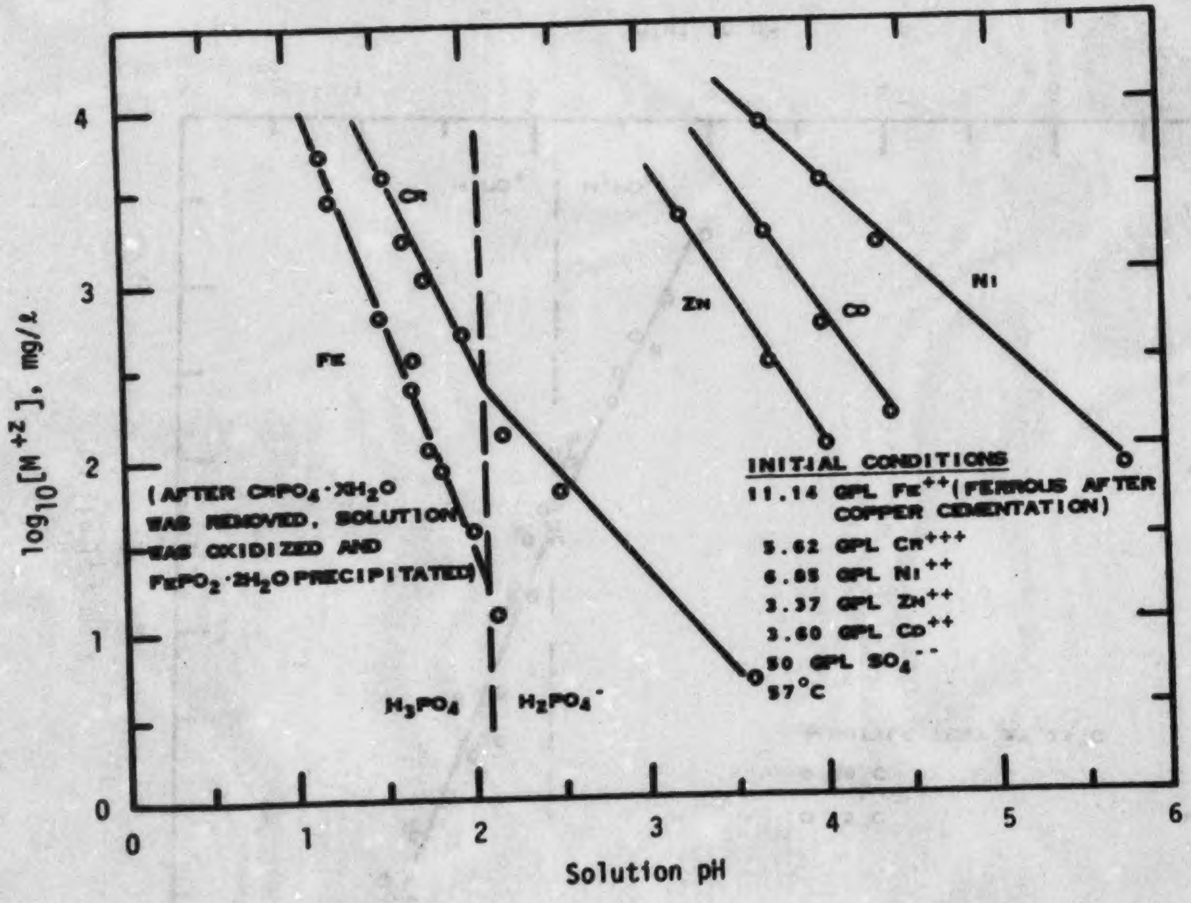

FIGURE 6.5. SELECTIVE REMOVAL OF CHROMIUM AND IRON FROM DIVALENT CATIONS IN ELECTROPLATING SLUDGE LEACH SOLUTIONS

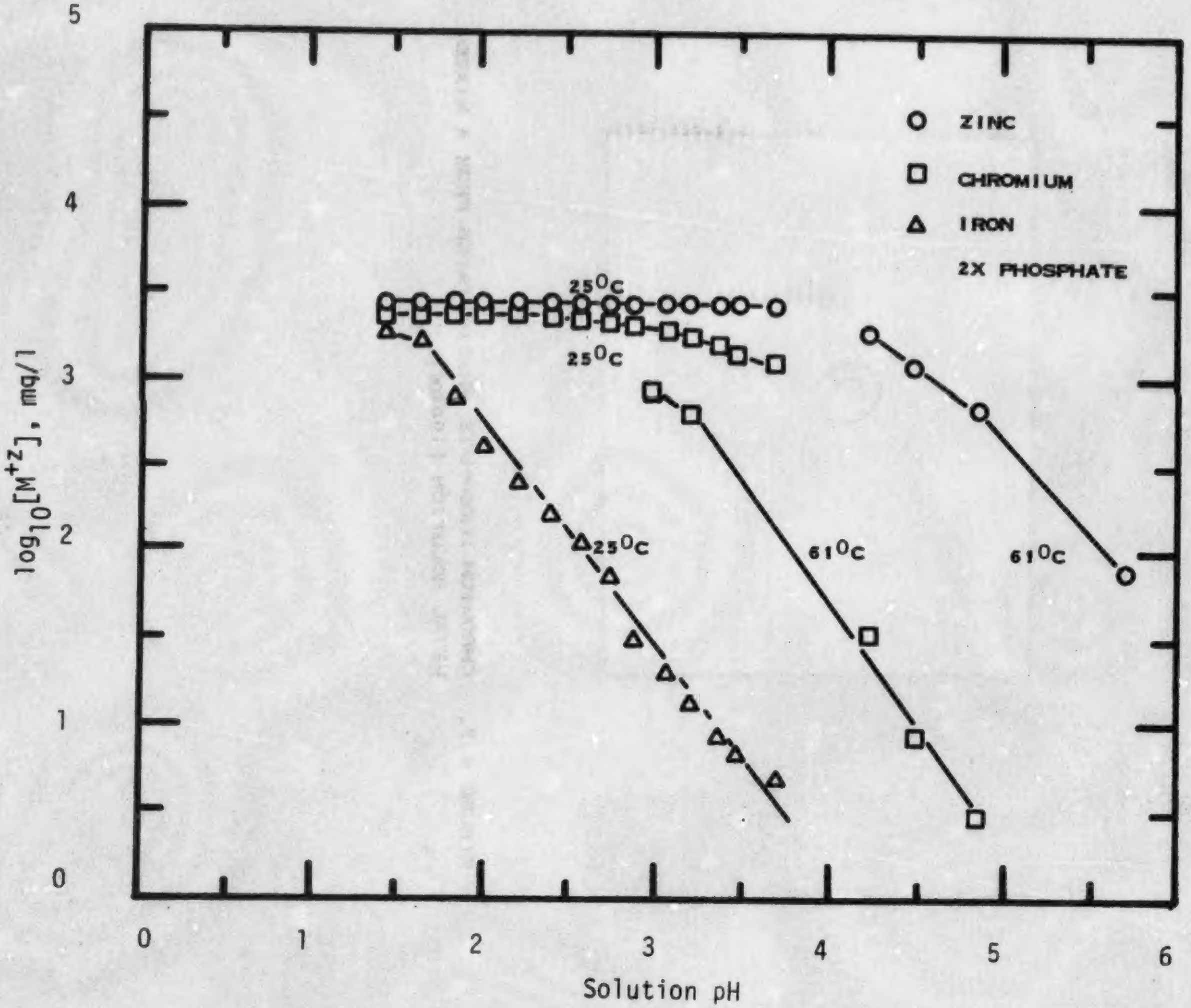

FIGURE 6.6. SELECTIVE PRECIPITATION OF IRON, CHROMIUM, AND ZINC

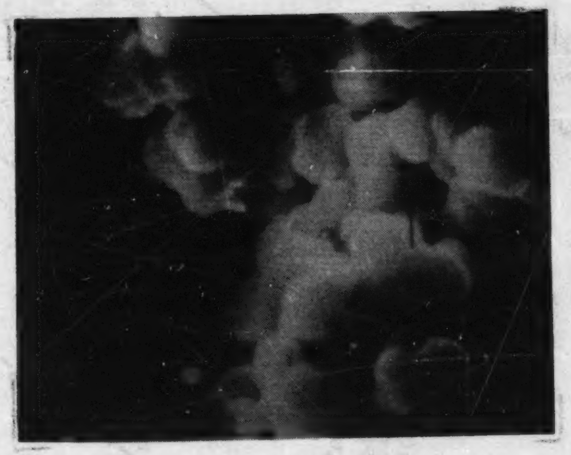

FIGURE 6.7. CHROMIUM PHOSPHATE PRECIPITATED FROM A MIXED METAL SOLUTION (1000X).

- Chromium phosphate precipitation is very temperature dependent. Room temperature precipitation does not occur until the solution pH is raised to at least 3.5 (in a one-hour time interval between pH adjustments), Figure 6.8.

  The influence of temperature on the precipitate solubility curve is very important because it allows iron to be stripped at room temperature from an iron-chromium solution by controlling the pH below 3.5 for one-half to one hour; filtering the iron phosphate from the solution; then precipitating the chromium by raising the temperature to 50-80°C.

- Precipitation is rapid (0.5-1 hr.), effective (<10 mg/liter) and selective over divalent cations such as zinc, cadmium, and nickel at a pH of 3.5 at 57°C, Figure 6.5; and at 61°C and 83°C, Figure 6.9.

- Filterability of the high temperature chromium phosphate is excellent, i.e., about the same as ferric phosphate.

A number of different flowsheets can be formulated to treat a given sludge material. However, a common feature of most of the visualized flowsheets is that iron must be removed first, then chromium. Divalent metals can also be removed by phosphate precipitation but other hydrometallurgical unit operations are available and may be used depending on the desired final product.

A great deal of emphasis has been given to separation of the trivalent cations of iron and chromium from mixed metal solutions because their removal is necessary before the other valuable metals can be recovered without iron and/or chromium contamination:

- the removal of iron from mixed metal solutions is a high cost unit operation (1) if done by high temperature jarosite precipitation, solvent extraction, or hydroxide precipitation.

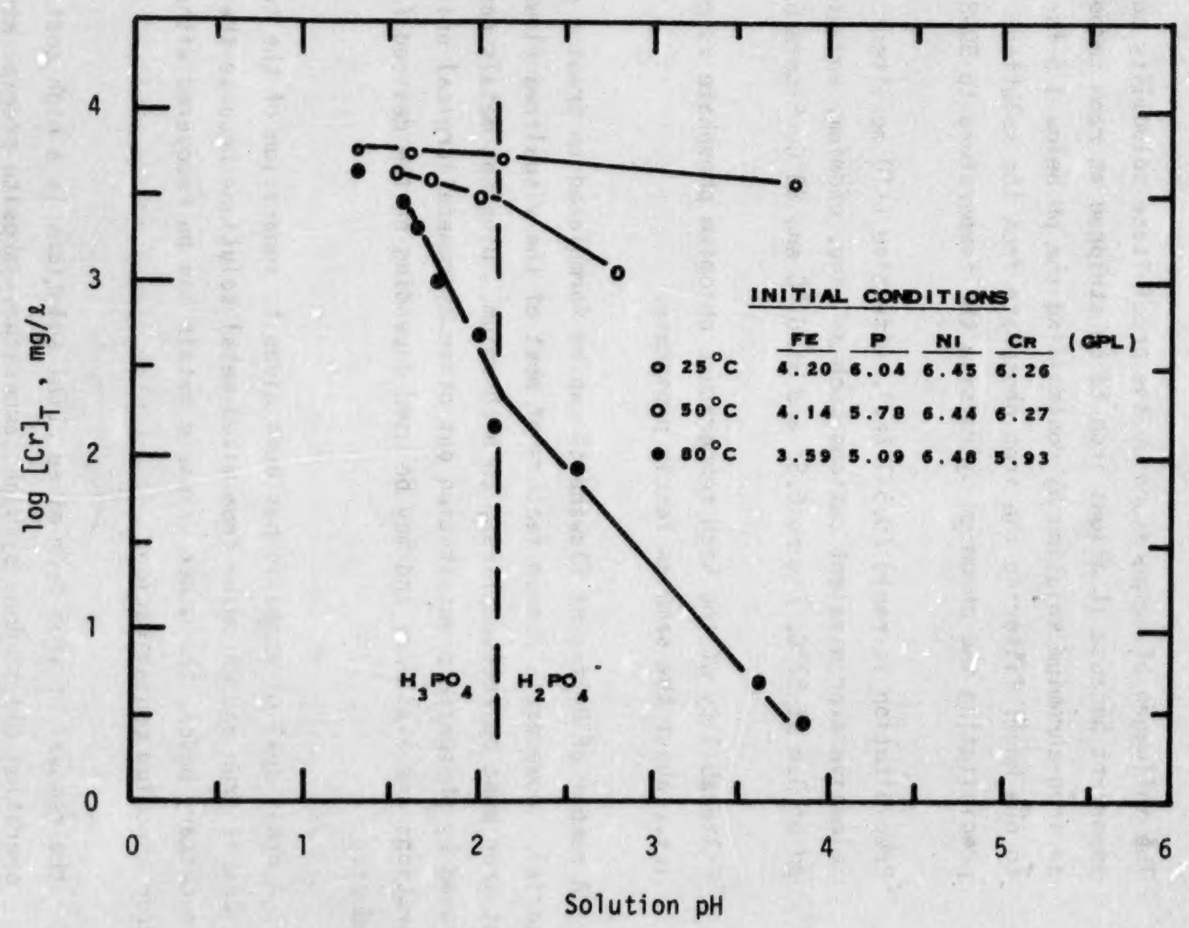

FIGURE 6.8. INFLUENCE OF TEMPERATURE ON CHROMIUM PHOSPHATE PRECIPITATION FROM A MIXED METAL SOLUTION

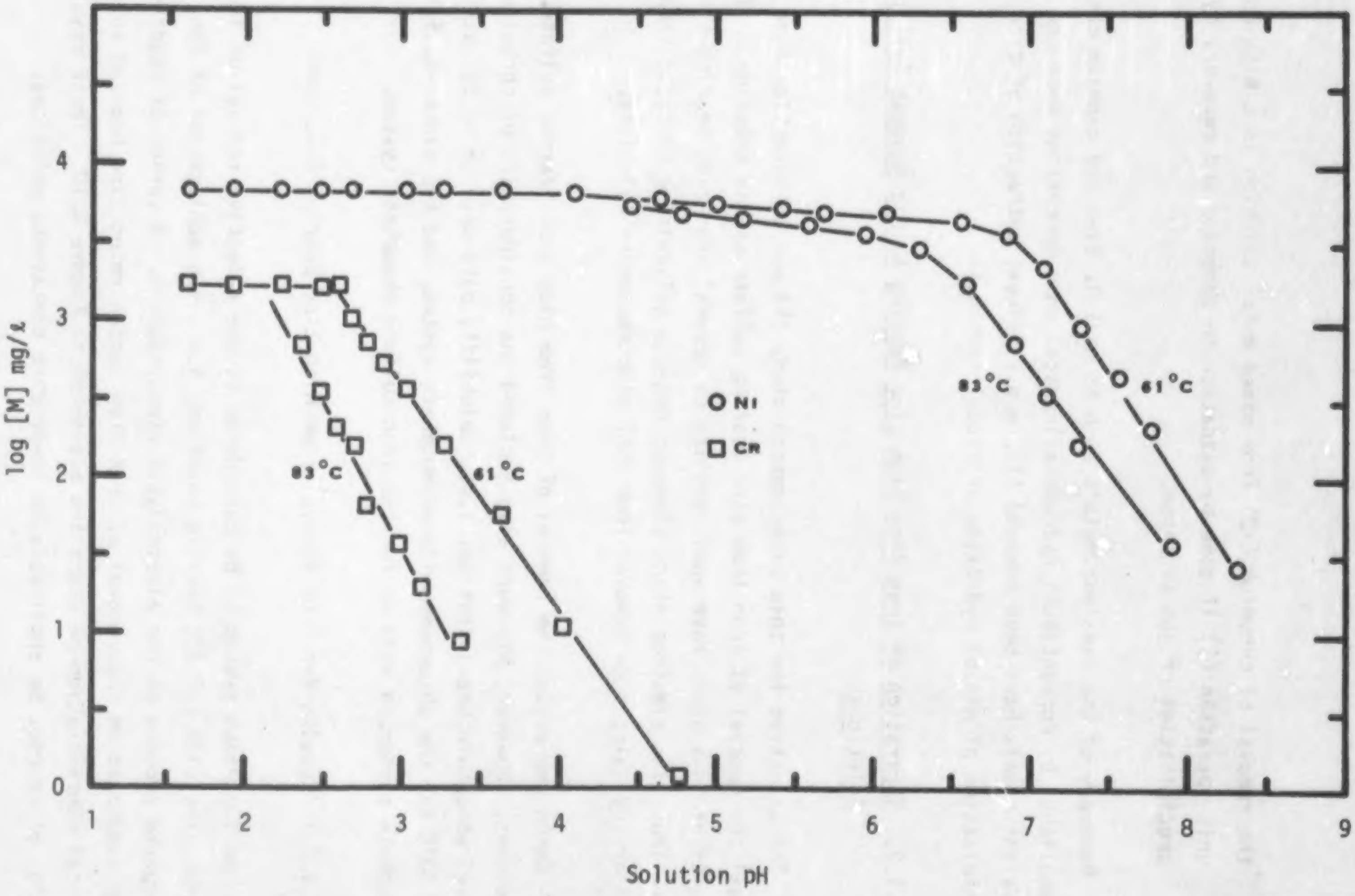

FIGURE 6.9. SELECTIVE SEPARATION OF CHROMIUM AND NICKEL

- the removal of chromium (+3) from mixed metal solution is a high cost unit operation (1) if done by oxidation to chromate and recovery by precipitation or ion exchange.

Recovery of the divalent metals such as nickel, zinc and cadmium can be accomplished by conventional hydrometallurgical unit operations once the trivalent metals have been removed (1), e.g., solvent extraction of zinc and precipitation of nickel hydroxide or nickel carbonate.

6.1.1.2. Separation of Iron from High Zinc Bearing Acidic Aqueous Sulfate Solutions

The objective for this experimental study (9) was to investigate in detail the removal of iron from zinc bearing sulfate matrix solutions. The results of this study have applicability to several iron-zinc bearing sludges, e.g., iron-zinc electroplating sludges; hot-dip galvanizing sludges; iron-zinc chiller crystals; iron removal from zinc electrowinning solutions.

Konda emphasized the removal of iron from high zinc bearing sulfate solutions. However, his work also included the consideration of chromium and nickel phosphate precipitation, i.e., solubility data were collected at 25°C and 50°C for the chromium-sulfate-phosphate system, and the nickel-sulfate-phosphate system, a well as for the iron-sulfate-phosphate system.

6.1.1.2.1 Results for Iron Removal from High Zinc Bearing Solutions

An important system to be considered is the selective removal of iron from a high zinc (125 gpl Zn) bearing solution, i.e., the application of the phosphate process to the electrolytic zinc industry. A series of studies have been conducted on the removal of iron from concentrated zinc bearing solutions. Typical concentration-pH scans are presented in Figure 6.10. These results would, of course, be applicable to lower zinc containing solutions.

Solids were collected from the solution (Figure 6.10, 2X curve) at various pH levels, dissolved and analyzed. The results are presented in

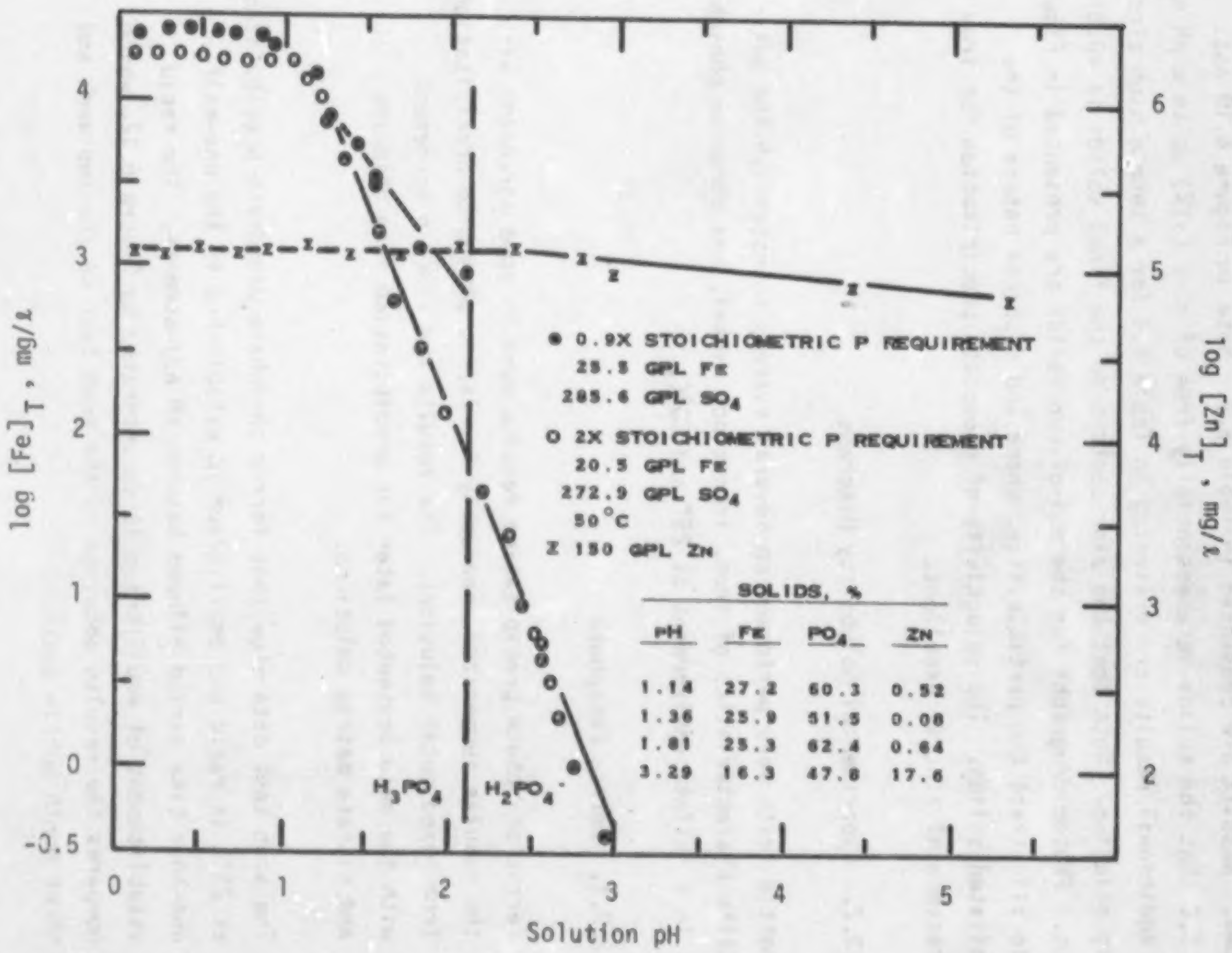

FIGURE 6.10. THE PRECIPITATION OF IRON PHOSPHATE FROM A HIGH ZINC BEARING SOLUTION.

Figure 6.10. Solids (produced at various pH values) were also analyzed by SEM-EDAX. Results are presented in Table 6.2. Note in Figure 6.10 and Table 6.2 that the solids were essentially free of zinc (<1%) up to a pH of 1.8. Additional results are presented in Table 6.3 for a second high zinc bearing solution. Note that the zinc content in the final solids is <0.81 percent. Photomicrographs for the end-of-run solids are presented in Figure 6.11 to illustrate the particle size, shape and discrete nature of the precipitated solids. The selectivity of phosphate precipitation for iron in the presence of zinc is excellent.

6.1.1.2.2. Experimental Solubility Diagrams

Bottle tests were performed on several systems to establish the basic solubility characteristics of iron, iron-zinc, nickel, and chromium phosphate solids in a sulfate environment at 25° and 50°C.

6.1.1.2.2.1. Ferric Phosphate

- Ferric phosphate precipitation results were in good agreement with the results summarized previously for ferric phosphate precipitation from mixed metal solutions. The results are also in agreement with the data presented later for precipitation from chloride and nitrate matrix solutions.

- The scan test data show that ferric phosphate dihydrate precipitation at 25°C is rapid and equilibrium is established in the one-half - one-hour time period allowed between pH adjustments. The rapid establishment of equilibrium is demonstrated by Figure 6.12, which compares the results obtained by the scan test to the two week and three month bottle tests.

- As was discussed earlier the solubility of ferric phosphate dihydrate is not a function of temperature to at least above 50°C. This result is confirmed by the present thesis research, Figure 6.13. The conclusion holds true even in a high zinc bearing solution.

TABLE 6.2. ZINC CONTENT IN PRECIPITATED FERRIC PHOSPHATE PRODUCED FROM A HIGH ZINC BEARING SOLUTION

Solution pH	Zinc Content in Solids (%)
1.36	0.5
1.66	0.5
2.46	1.7
2.93	9.9
2.96	9.3
5.20	23.3

Starting solution composition (gpl): 150 Zn, 20.5 Fe, 28.8 P, 272.9 SO_4.
Temperature 50°C.

TABLE 6.3. COMPOSITION OF SOLIDS FROM END-OF-RUN IRON-ZINC-SULFATE SYSTEM

	Solids Composition (%)	
	ICP	SEM-EDAX
Fe	30.56	32.08
P(as PO_4)	49.31	47.87
H_2O	19.06	19.08
Zn	0.60	0.81
Na	0.84	——
S	——	0.15

Test conditions: Starting composition (gpl): 22.80 Fe, 77.46 Zn, 27.24 P, 57.83 S (172.8 SO_4); temperature 53°C; end-of-run pH 1.46; end-of-run iron content in solution 88 mg/liter.

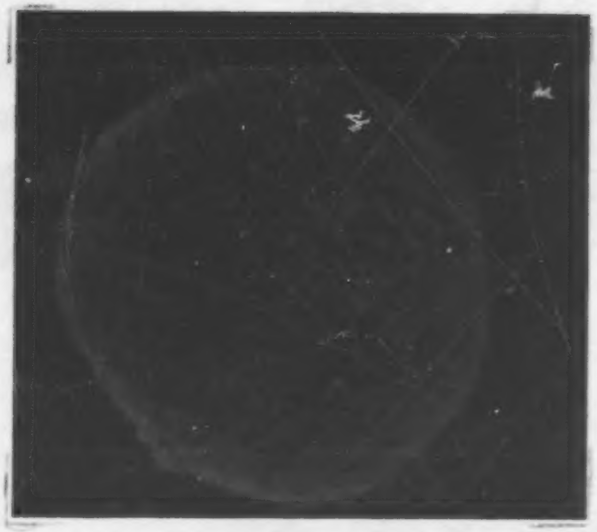

FIGURE 6.11. PHOTOMICROGRAPHS OF SOLIDS PRODUCED FROM A HIGH ZINC BEARING SOLUTION (360X, 1000X)

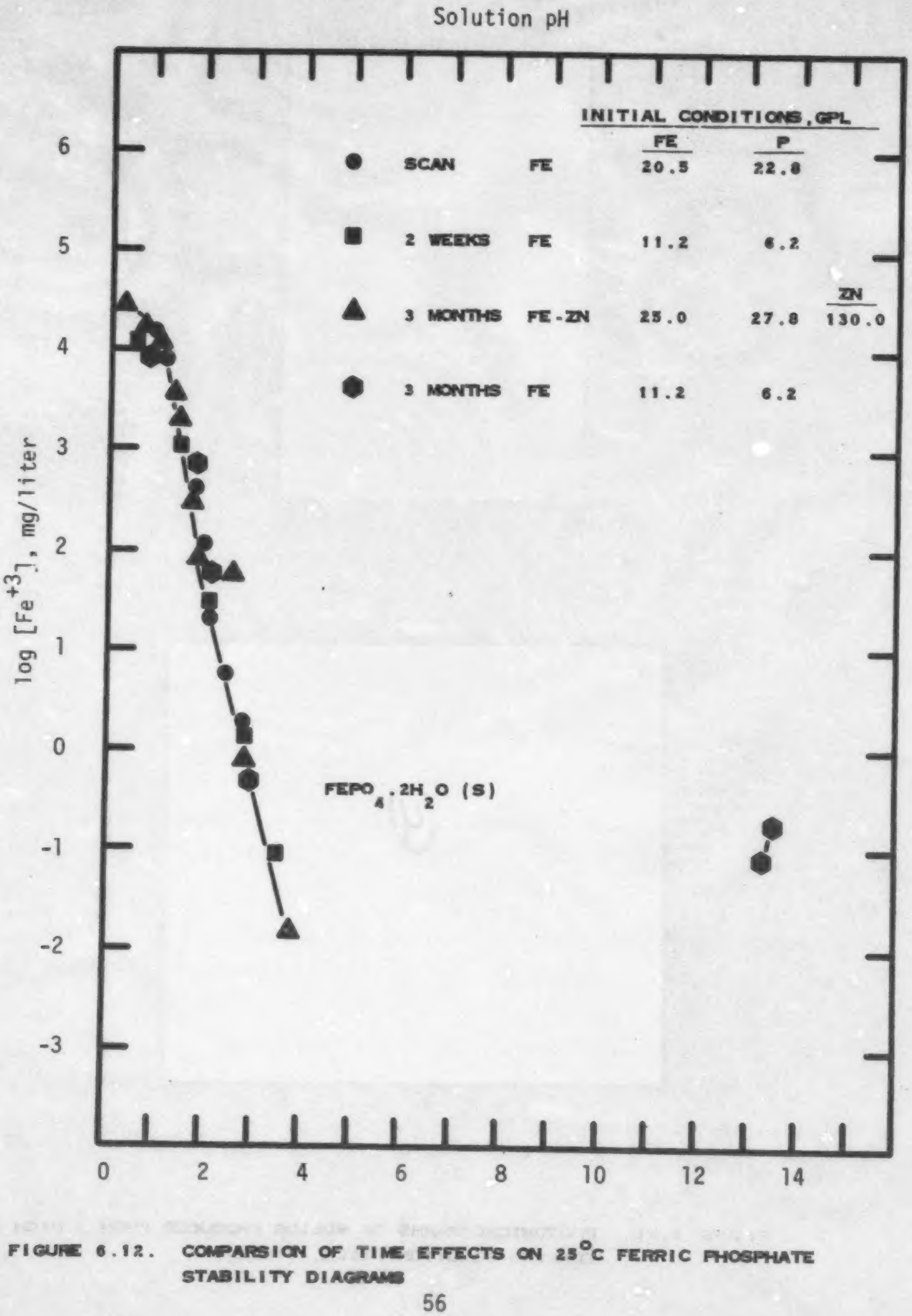

FIGURE 6.12. COMPARSION OF TIME EFFECTS ON 25°C FERRIC PHOSPHATE STABILITY DIAGRAMS

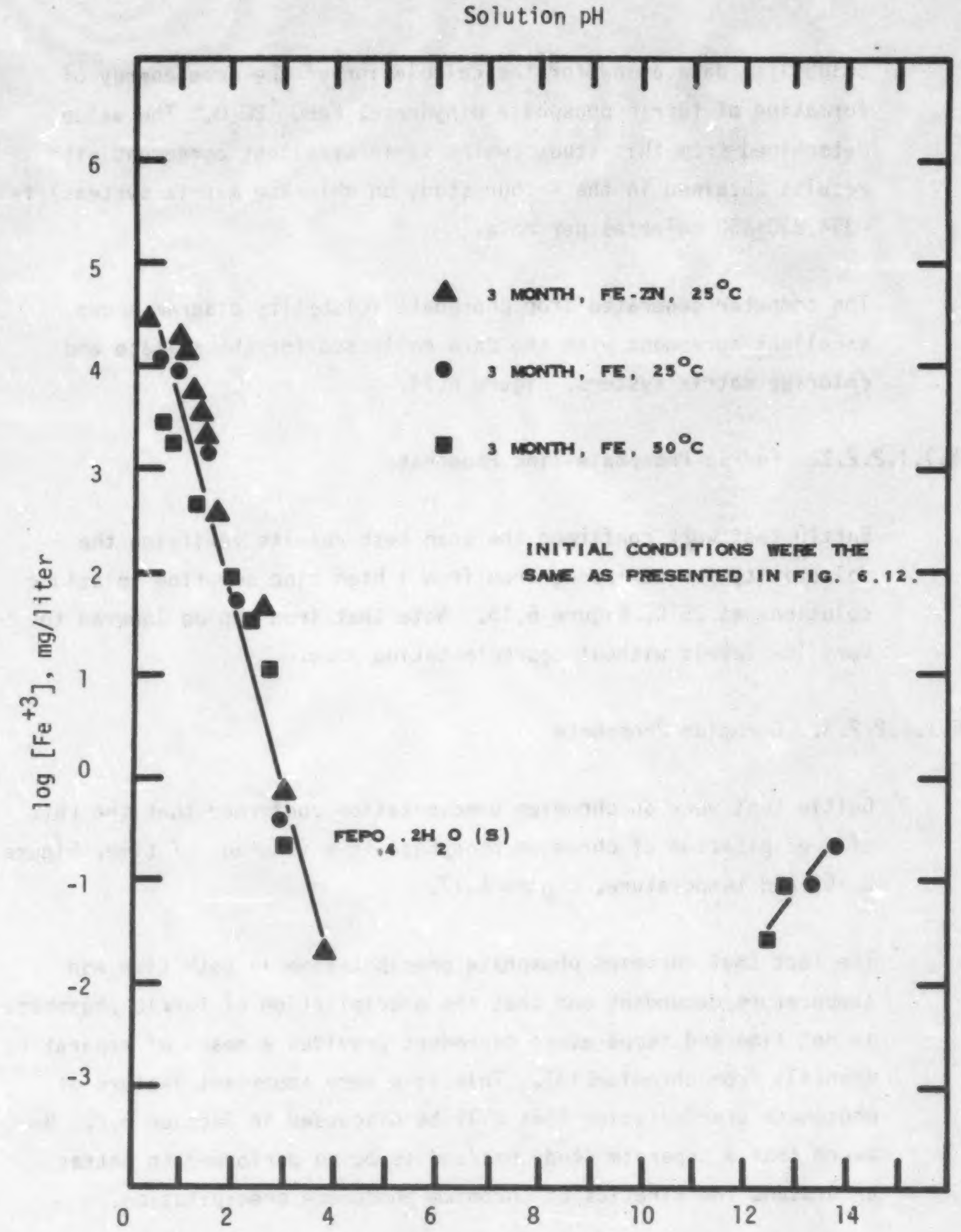

FIGURE 6.13. COMPARISON OF THREE MONTH TEMPERATURE EFFECTS ON FERRIC PHOSPHATE STABILITY DIAGRAMS

- Solubility data allow for the calculation of the free energy of formation of ferric phosphate dihydrate, $FePO_4 \cdot 2H_2O$. The value determined from this study (which is in excellent agreement with results obtained in the Arthur study on chloride matrix systems) is $-394,830 \pm 850$ calories per mole.

  The computer generated iron phosphate solubility diagram shows excellent agreement with the data collected for the sulfate and chloride matrix systems, Figure 6.14.

6.1.1.2.2.2. Ferric Phosphate-Zinc Phosphate

- Bottle test work confirmed the scan test results verifying the selectivity for stripping iron from a high zinc solution in acidic solutions at 25°C, Figure 6.15. Note that iron can be lowered to very low levels without coprecipitating zinc.

6.1.1.2.2.3. Chromium Phosphate

- Bottle test work on chromium precipitation confirmed that the rate of precipitation of chromium phosphate is a function of time, Figure 6.16; and temperature, Figure 6.17.

- The fact that chromium phosphate precipitation is both time and temperature dependent and that the precipitation of ferric phosphate is not time and temperature dependent provides a means of separating iron(+3) from chromium(+3). This is a very important feature of phosphate precipitation that will be discussed in Section 6.2. Be aware that a separate study has/and is being performed to better understand the kinetics of chromium phosphate precipitation.

6.1.1.2.2.4. Nickel Phosphate

- Precipitation of nickel phosphate is similar to chromium phosphate.

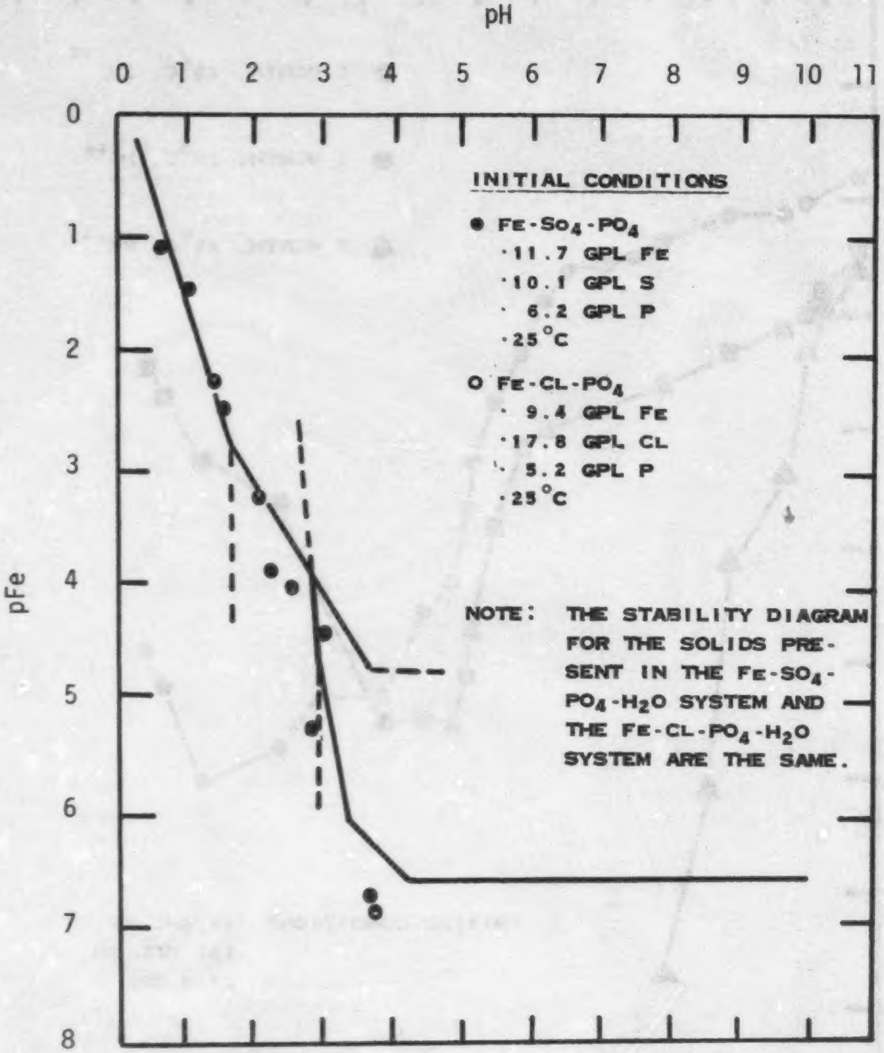

FIGURE 6.14 EXTENDED TIME EXPOSURE TESTS FOR THE IRON-PHOSPHATE-CHLORIDE-WATER SYSTEM AT 25°C.

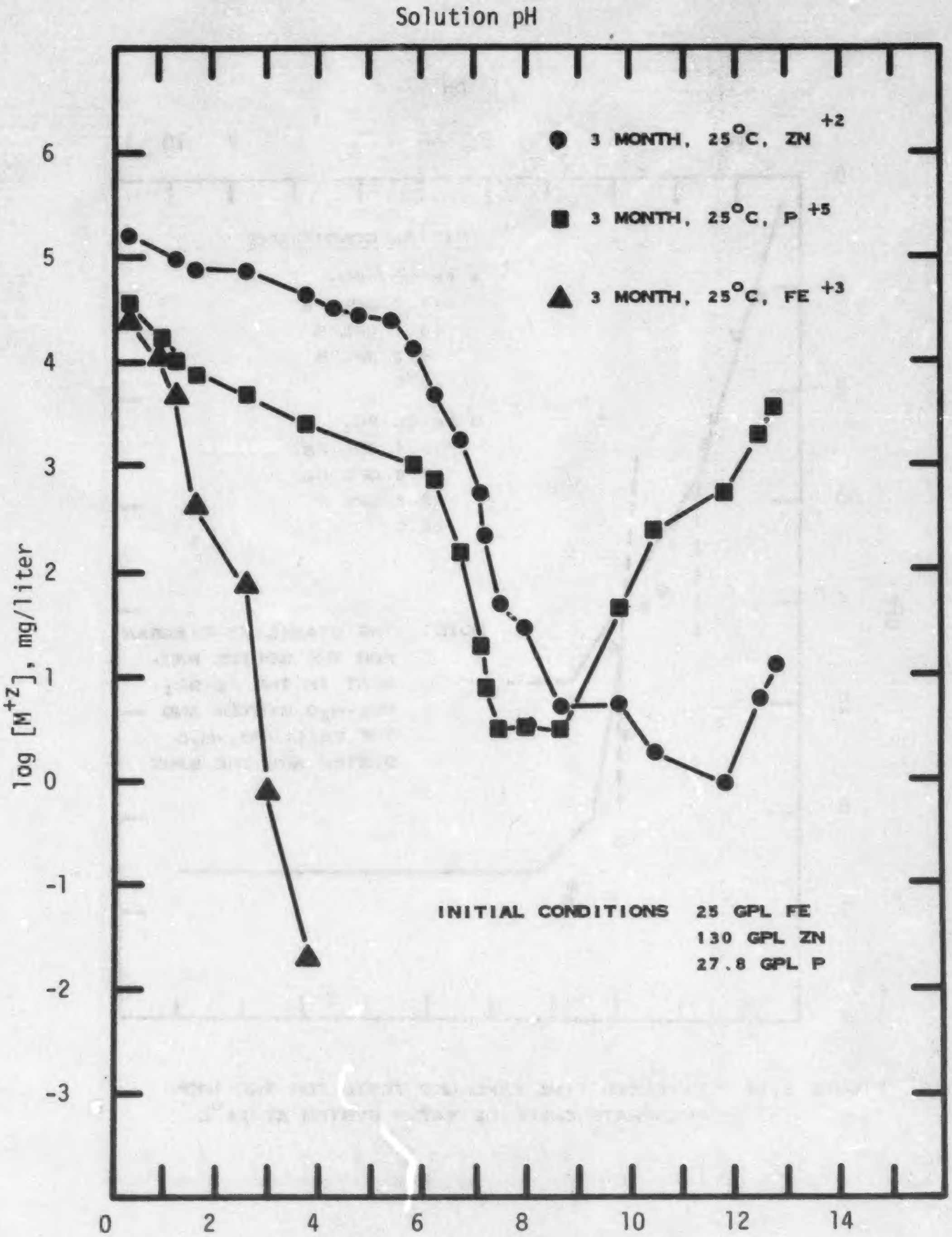

FIGURE 6.15. COMPARISON OF THREE MONTH PHOSPHATE STABILITY DIAGRAMS FOR 25°C IRON AND ZINC SYSTEM

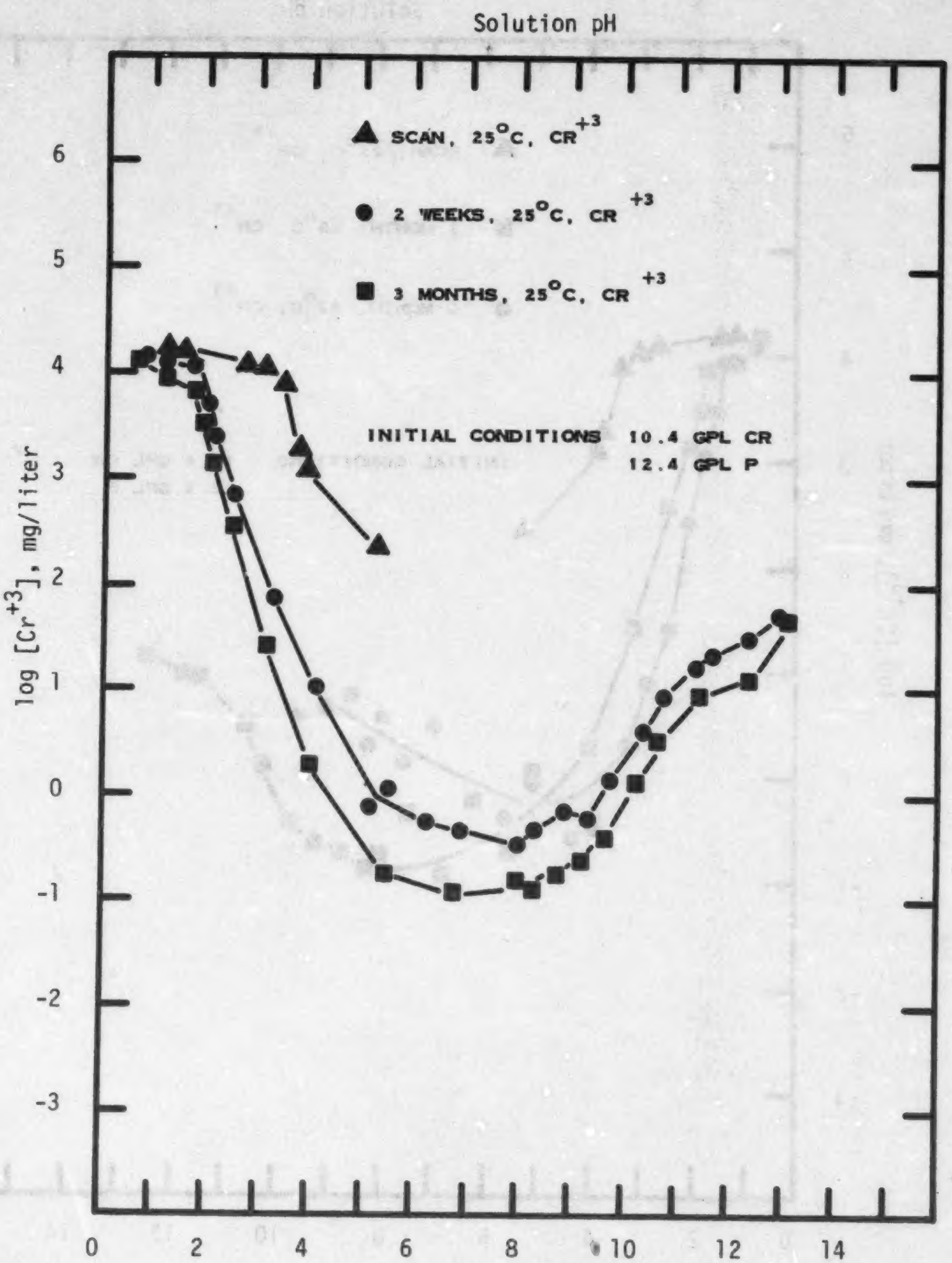

FIGURE 6.16. COMPARSION OF TIME EFFECTS ON 25°C CHROMIUM PHOSPHATE STABILITY DIAGRAMS

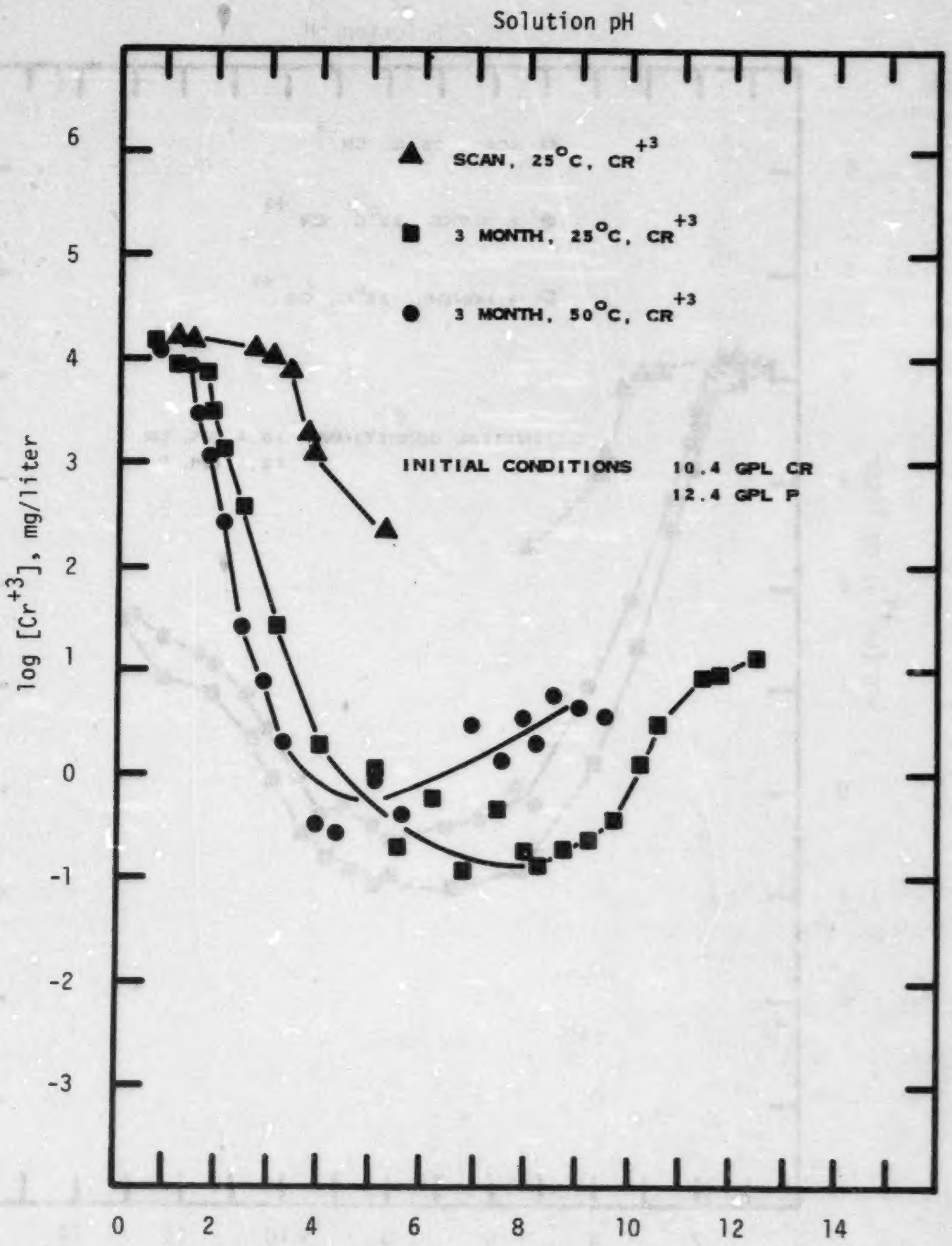

FIGURE 6.17. COMPARISON OF THREE MONTH TEMPERATURE EFFECTS ON CHROMIUM PHOSPHATE STABILITY DIAGRAMS

i.e., it is a time dependent precipitation, Figure 6.18. This is a very important feature because it may be possible to selectively precipitate ferric iron from a nickel(+2) solution at higher pH levels than would be predicted from the computer generated solubility diagrams.

- Although the results are somewhat scattered at pH levels above seven, comparsion of Figure 6.18 and 6.19 shows that precipitation of nickel phosphate is temperature dependent in aqueous solutions.

6.1.1.3. Separation of Iron, Chromium, and Nickel from Aqueous Chloride Solutions

The objective of this study was to investigate the precipitation of iron phosphate, chromium phosphate and nickel phosphate from chloride and nitrate matrix solutions. Pure metal systems were investigated. Also selective separations from mixed metal sludge leach solutions were investigated.

A large quantity of data was generated by this study (10). In general the conclusion is that selective separations can be made from chloride solutions just as effectively as from sulfate solution. The phosphate compounds precipitate similarly in both solvent systems with respect to pH, time and temperature. The results are summarized in the following sections.

6.1.1.3.1. Ferric Phosphate

The experimental results of Arthur (10) can be summarized with respect to ferric phosphate precipitation as follows:

- Precipitated particle morphology is similar to that obtained from sulfate solutions, i.e., small spherites and agglomerates of spherites, Figure 6.20. The filterability of the precipitated ferric phosphate is excellent, Table 6.4. Ferric phosphate filters very

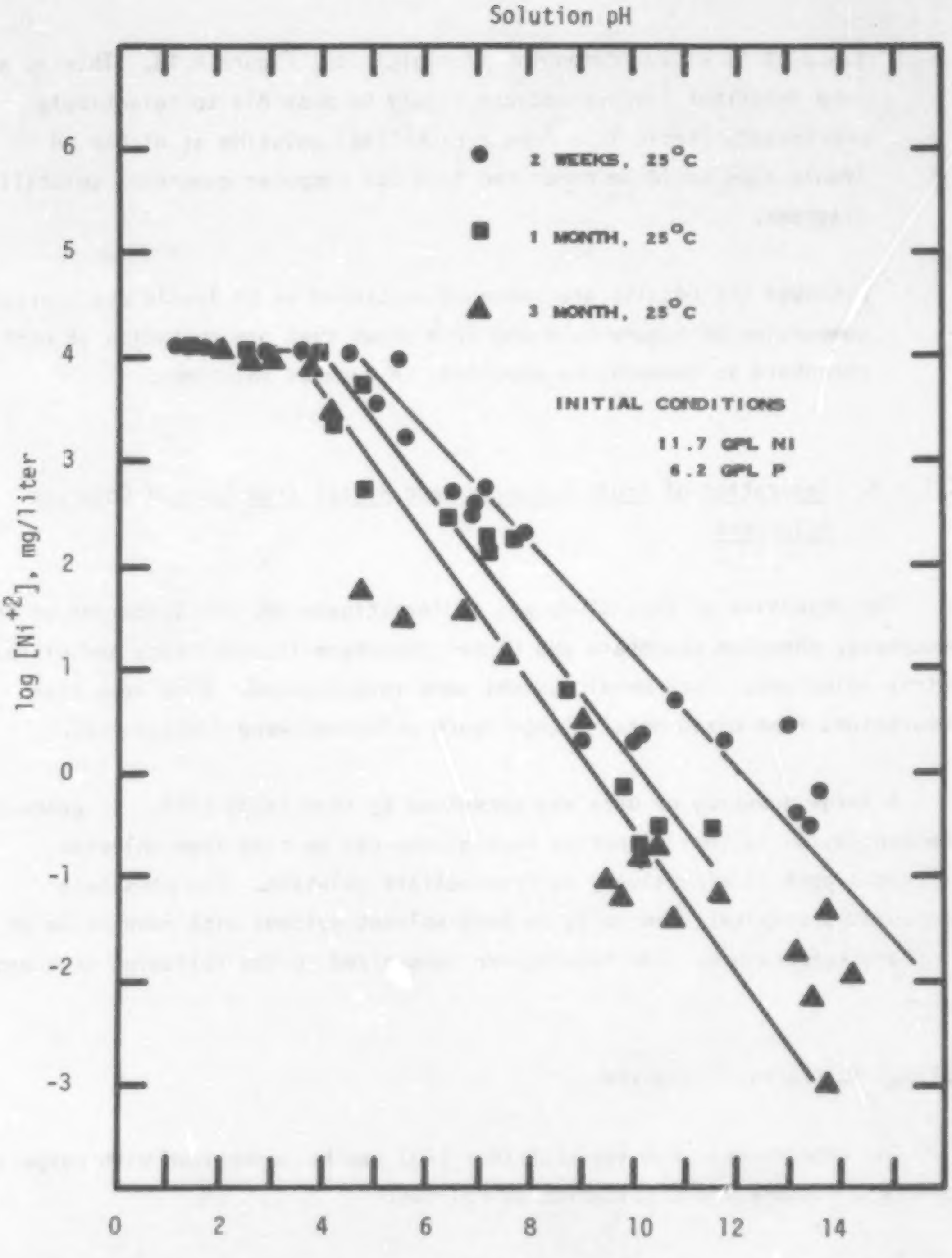

FIGURE 6.18. COMPARISON OF TIME EFFECTS ON 25°C NICKEL PHOSPHATE STABILITY DIAGRAMS

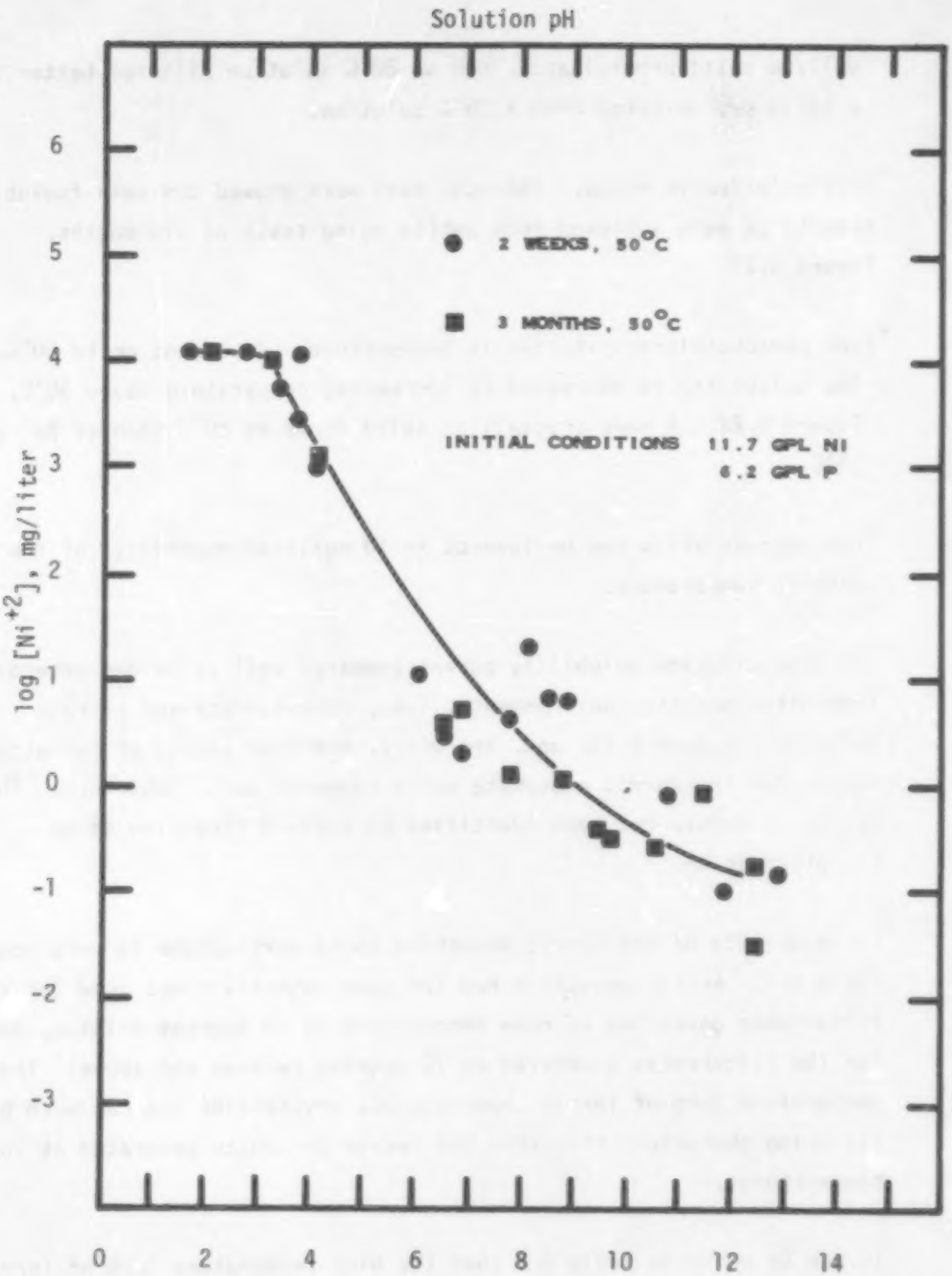

FIGURE 6.19. COMPARSION OF TIME EFFECTS ON 50°C NICKEL PHOSPHATE STABILITY DIAGRAMS

well; a solid precipitated from an 80°C solution filtered better than a solid precipitated from a 25°C solution.

- Precipitation is rapid. The scan test work showed the same fsolubility results as were achieved from bottle aging tests of six months, Figure 6.21.

- Iron phosphate precipitation is temperature independent up to 50°C. The solubility is decreased by increasing temperature above 50°C, Figure 6.22. A more crystalline solid forms at 80°C than at 50° or 25°C.

- Iron concentration can be lowered to 10 mg/liter regardless of the solution temperature.

- The precipitation solubility curves compared well to values determined from other solution environments, i.e., from sulfate and nitrate solutions, Figure 6.23, and, therefore, the free energy of formation values for the ferric phosphate solid compares well, Table 6.5. The ferric phosphate has been identified by X-ray diffraction to be phosphosiderite.

- Filterability of the ferric phosphate solid particulate is very good, Table 6.4. Ferric phosphate had two cake resistivities: one for the filtercakes generated at room temperature to 70 degrees celsius, and one for the filtercakes generated at 70 degrees celsius and above. The high temperature form of ferric phosphate was crystalline and had much better filtering characteristics than the ferric phosphate generated at lower temperatures.

It can be noted in Table 6.4 that the high temperature form of ferric phosphate has a cake resistivity slightly better than that of

jarosite. This implies that ferric phosphate filters very well. Because the procedure used to test jarosite was a reslurry, its

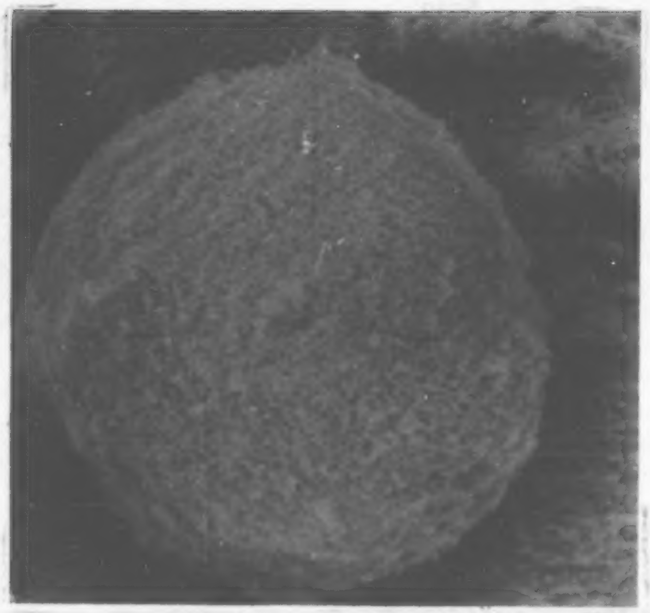

FIGURE 6.20. SEM PHOTOMICROGRAPH OF ROOM TEMPERATURE PRECIPITATED FERRIC PHOSPHATE (310X)

TABLE 6.4. A LIST OF FILTERABILITY RESULTS FOR VARIOUS COMPOUNDS

Sample	Compound	Conditions	Slope	C-Value	R_{cake}
7009	$FePO_4$	Room Temp., pH Scan	1.12E-3	0.0325	3.4E+10
7028	$FePO_4$	80°C, pH Scan	5.00E-5	0.0336	1.2E+9
7072	$FePO_4$	Noncrystalline	3.70E-4	0.0323	1.2E+10
7083	$FePO_4$	Crystalline 80°C	3.78E-4	0.0506	7.3E+9
7175	$CrPO_4$	Crystalline Room Temp.	3.00E-3	0.0736	1.4E+10
7183	$CrPO_4$	Noncrystalline, 50°C	3.00E-3	0.0609	5.7E+10
-	Jarosite	Reslurry	2.57E-4	0.0756	5.0E+9
5366	$Fe(OH)_3$	$FePO_4$ to $Fe(OH)_3$ conversion (2)	1.16E-2	0.0932	1.8E+11

Note: . For Comparsions refer to the R_{cake} column.

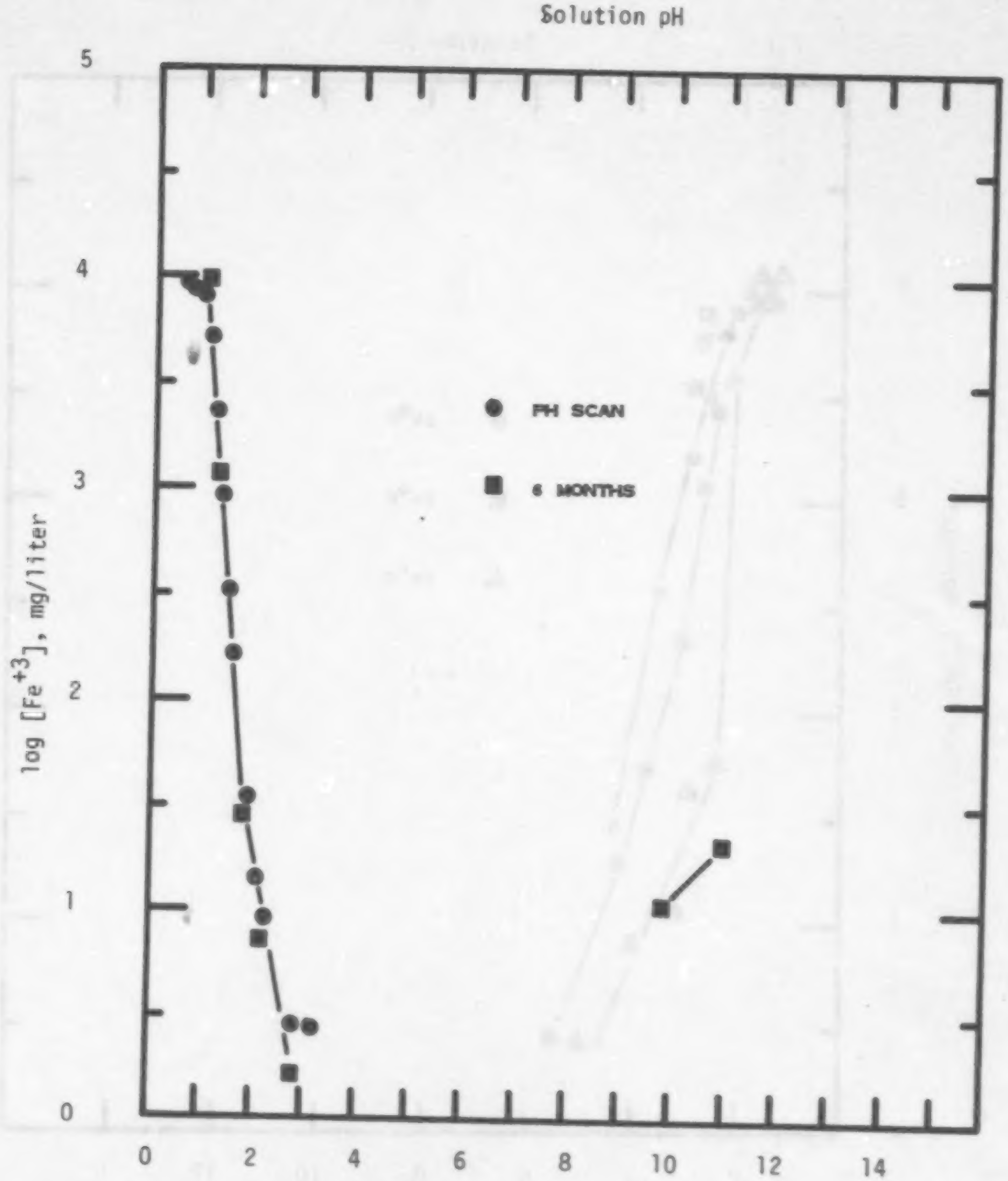

FIGURE 6.21. THE INFLUENCE OF TIME ON IRON REMOVAL FROM SOLUTION AS FERRIC PHOSPHATE

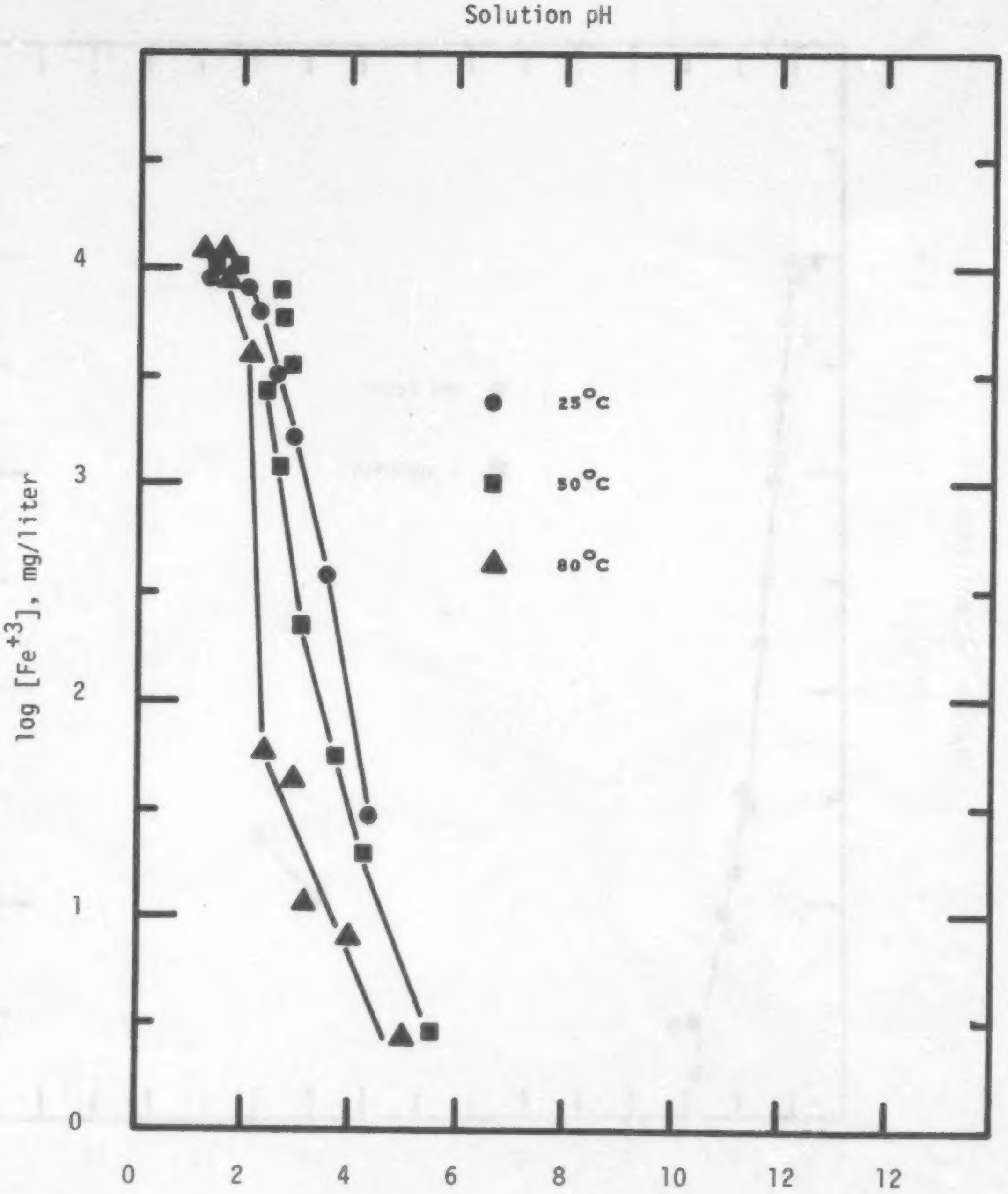

FIGURE 6.22. THE INFLUENCE OF TEMPERATURE ON IRON REMOVAL FROM SOLUTION AS FERRIC PHOSPHATE

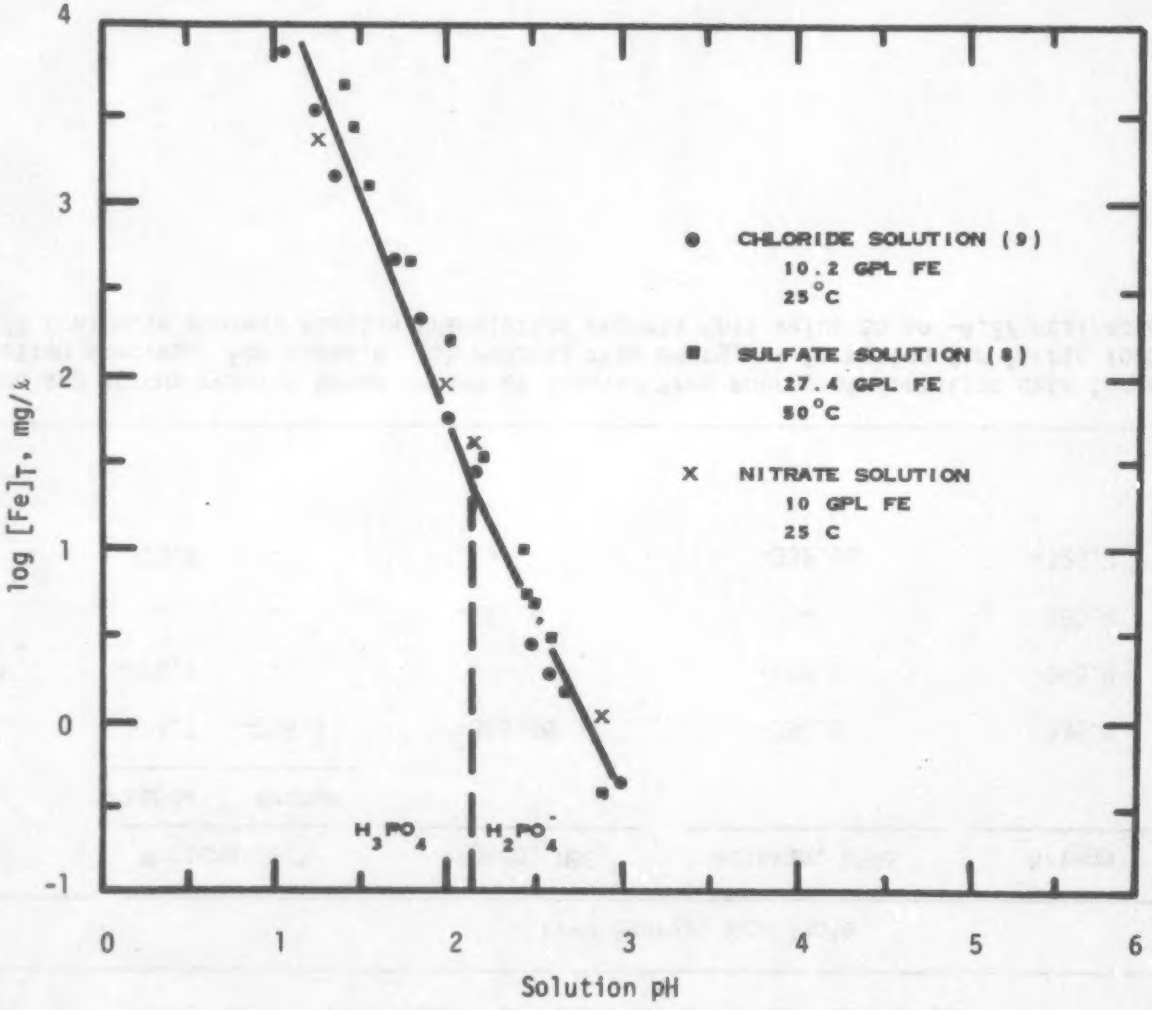

FIGURE 6 23. FERRIC PHOSPHATE PRECIPITATION FROM A CHLORIDE SULFATE, OR NITRATE SOLUTION

TABLE 6.5. FREE ENERGY OF FORMATION OF METAL PHOSPHATES

Phosphate	Free Energy, Kcal/mole				
	Montana Tech		Wagman, NBS	Russian, USGS	Nriagu
	Konda	Arthur			
$FePO_4 \cdot 2H_2O$	-394.7	-395.4	-396.16	-390.0	-396.0
$Zn_3(PO_4)_2 \cdot 4H_2O$	-870.7	-	-	-863.0	-866.9
$Ni_3(PO_4)_2$	-	-	-562.4	-	-560.8
$CrPO_4$	-323.4	-	-	-332.96	-325.7

Notes: Konda and Arthur results based on use of Russian free energy of formation data for aqueous solution species. For example, NBS reports free energy of formation for ferric ions to be -1.12 Kcal/mole whereas Russian translation reports this value to be -4.27 Kcal/mole.

filterability may be poorer than listed. This is because forming a precipitate produces a completely wet particle. When doing a reslurry of dry solids, it is very difficult to insure wetting is complete before a solid-liquid separation test is performed. If wetting was not complete, the actual resistivity would have been greater.

In order to observe a difference in filtering rates, a difference in resistivities of about one-half an order of magnitude is necessary. Thus, the difference between high temperature ferric phosphate and jarosite is not evident during a test; however, the difference between crystalline high temperature ferric phosphate and room temperature ferric phosphate is evident during a test.

In conclusion, any resistivity below 5.0E+10 is acceptable; any precipitate above 5.0E+10 is a poor filtering precipitate. This conclusion is based on test data which indicated that a filter cake with a resistivity of 5.0E+10 would require 15 minutes to filter one liter containing about 30 grams of dry solids under the following condition:

Area = 126 cm^2, P = 250mm Hg, Whatman #5 filter paper

The high temperature ferric phosphate and room temperature chromium phosphate would require as little as five minutes or less to filter one liter containing 30 grams of dry solids.

6.1.1.3.2. Chromium Phosphate

The experimental results of Arthur (10) can be summarized with respect to chromium phosphate precipitation as follows:

- Precipitated particle morphology is spherites, Figure 6.24.

- Chromium phosphate precipitation is very temperature dependent (as was

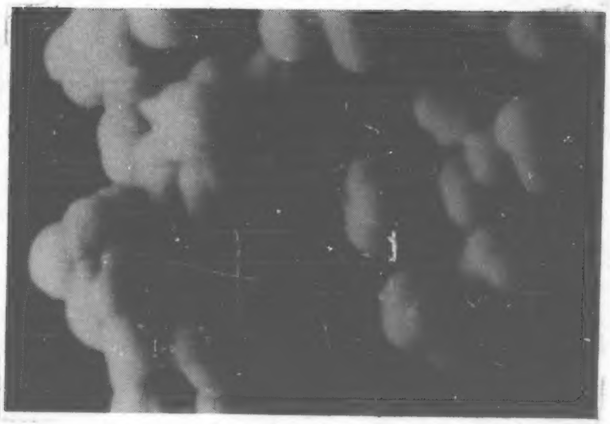

FIGURE 6.24. SEM PHOTOMICROGRAPH OF CHROMIUM PHOSPHATE PRODUCED AT ROOM TEMPERATURE (420X)

the case from a sulfate solution). Room temperature precipitation does not occur until the solution pH is raised to at least 3.3 (in a scan test), Figure 6.25.

- Scan test results at room temperature do not represent equilibrium solubility results. Solubility as a function of time curves were still shifting after three months, i.e, the six month data was significantly different from the three month data, Figure 6.26. The six-month data represent very well the quoted literature equilibrium data.

  As discussed previously, the influence of time on the precipitation solubility curve is very important and allows for good iron-chromium separations based on kinetics and temperature differences.

- The rate of precipitation is greatly enhanced by higher temperatures, i.e., note in Figure 6.27 that the solubility curve generated by a scan test at 80°C (one-half hour interval between pH adjustments) produces solubility levels essentially the same as long term (six months) bottle aging tests at room temperature.

6.1.1.3.3. Nickel Phosphate

The experimental results for removing nickel from chloride solutions can be summarized as follows:

- Only scan test work was performed on the nickel-chloride-phosphate system, i.e., bottle tests were not performed.

- Scan test results show that solid nickel phosphate did not occur until a pH of 4.51 was achieved (from a 10 gpl nickel solution) at 25°C, Figure 6.28.

- Nickel phosphate precipitation is very temperature dependent (as was the case from a sulfate solution), Figure 6.29.

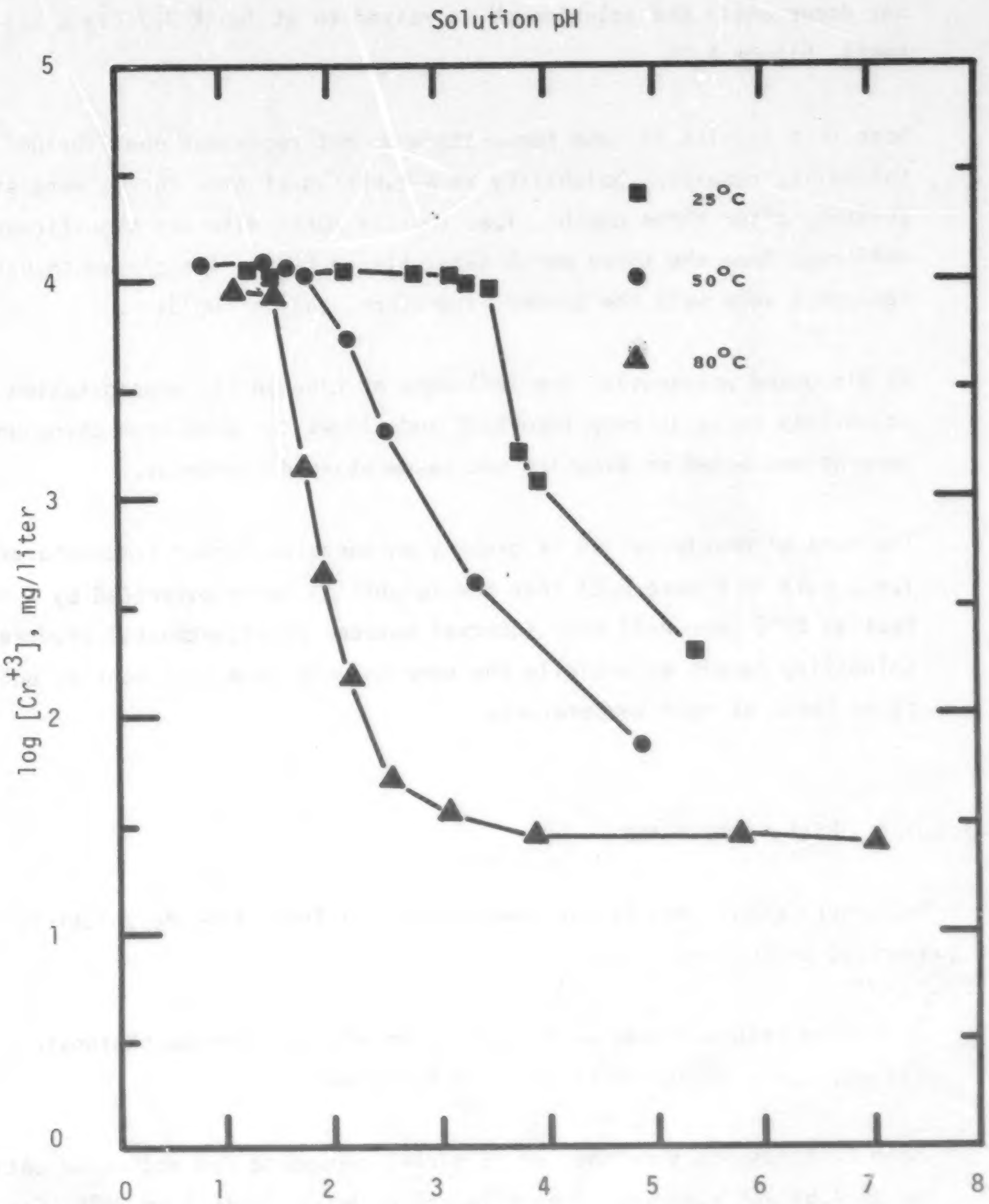

FIGURE 6.25. A COMPARISON OF SOLUBILITY CURVES FOR PH SCAN TESTS ON CHROMIUM SOLUTIONS AT ROOM TEMPERATURE, 50°C, AND 80°C

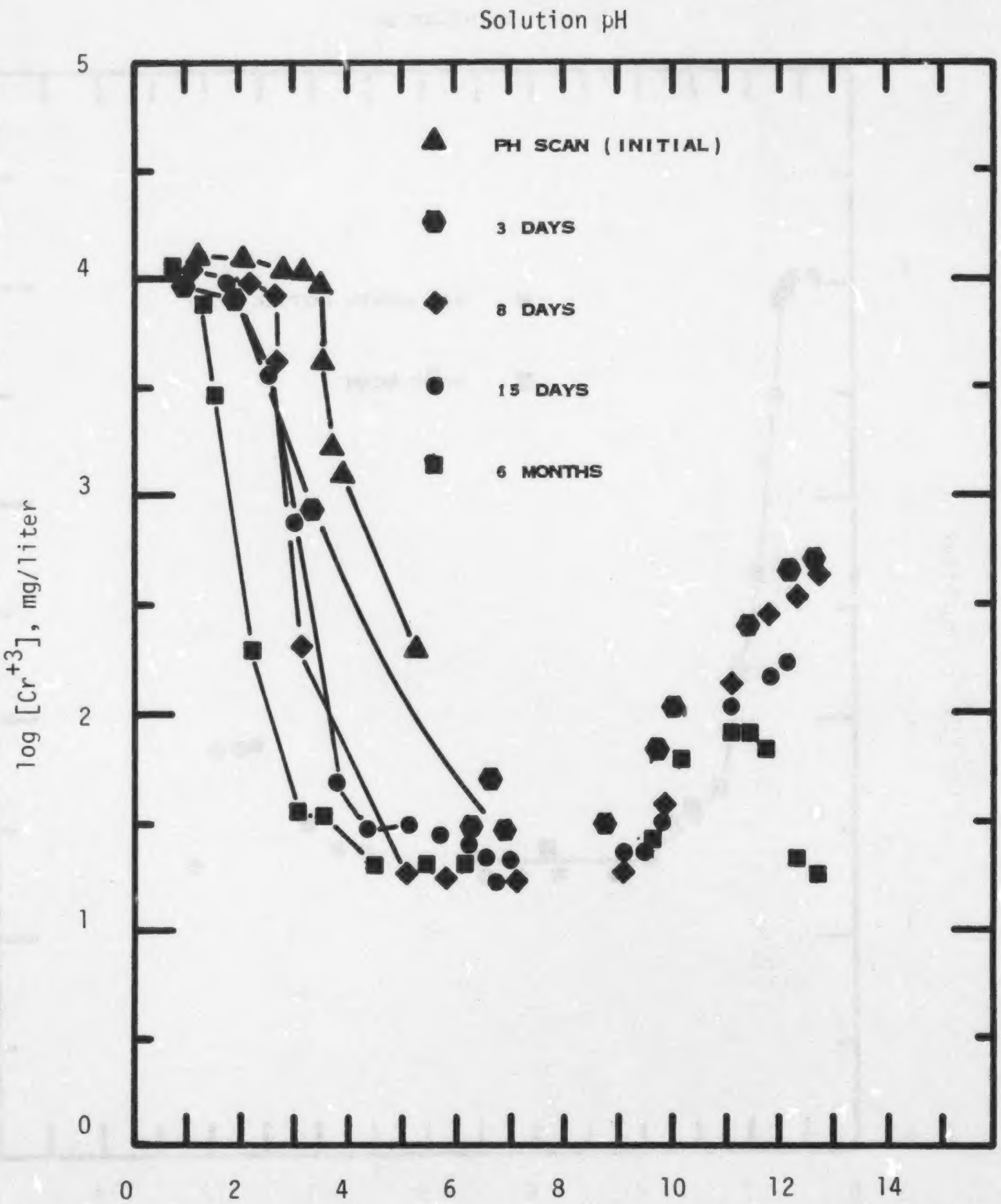

FIGURE 6.26. A COMPARSION OF SOLUBILITY CURVES FOR PH SCAN TESTS AS FUNCTION OF TIME FOR CHROMIUM SOLUTIONS

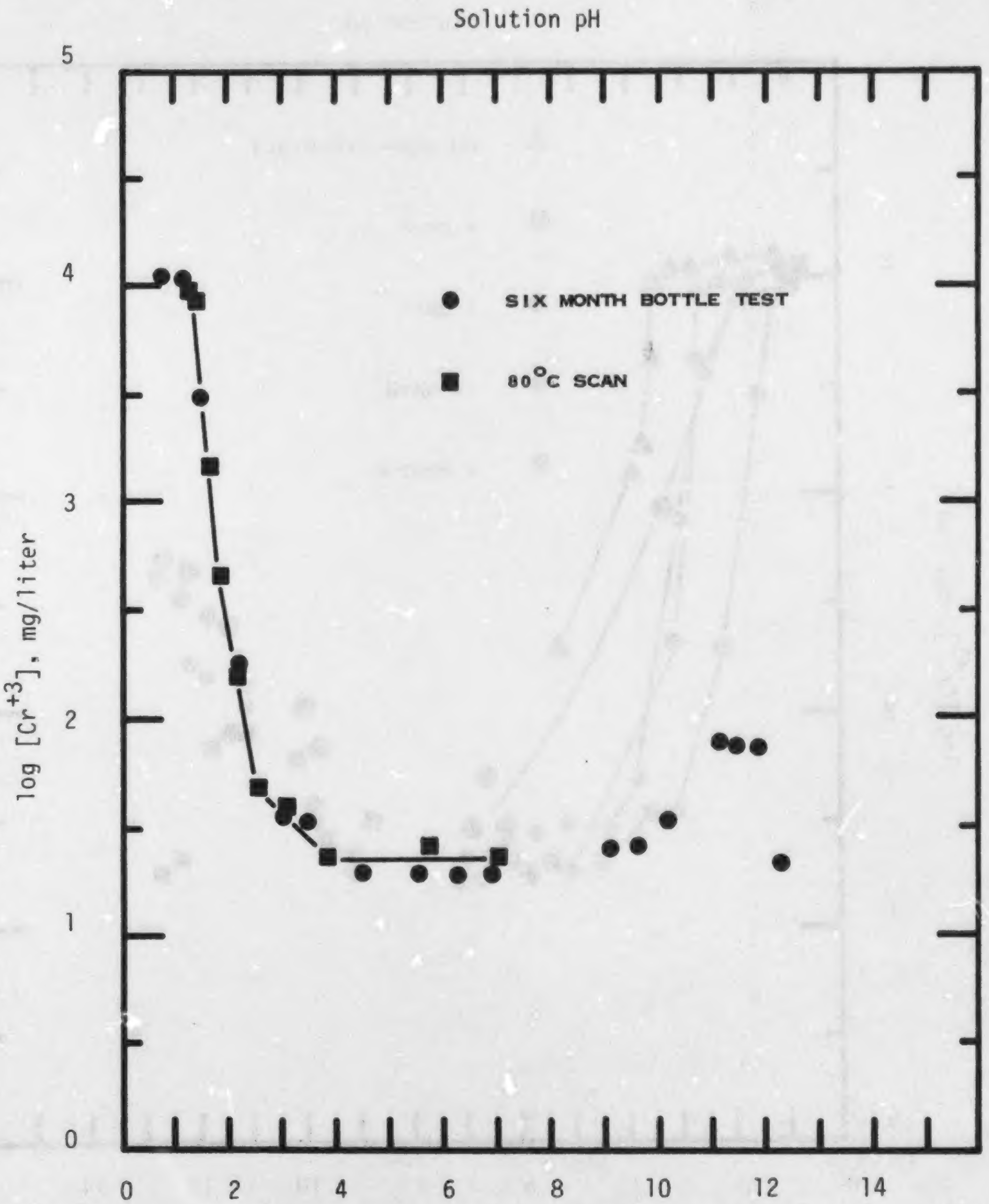

FIGURE 6.27. A COMPARSION BETWEEN CHROMIUM PHOSPHATE PRECIPITATION AT 80°C AND SIX MONTH BOTTLE TESTS

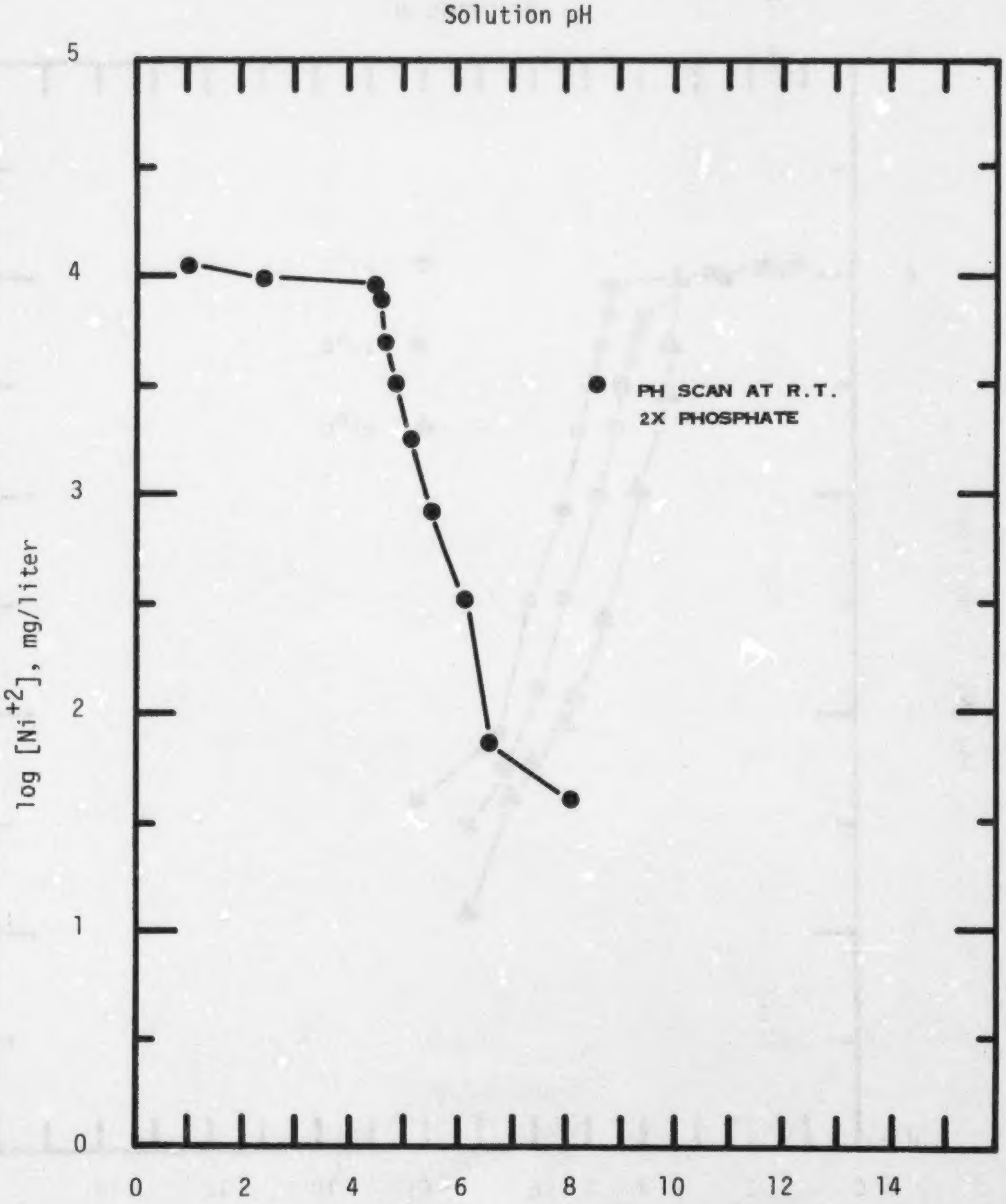

FIGURE 6.28. NICKEL PHOSPHATE PRECIPITATION FROM THE NICKEL-CHLORIDE-WATER SYSTEM AT ROOM TEMPERATURE

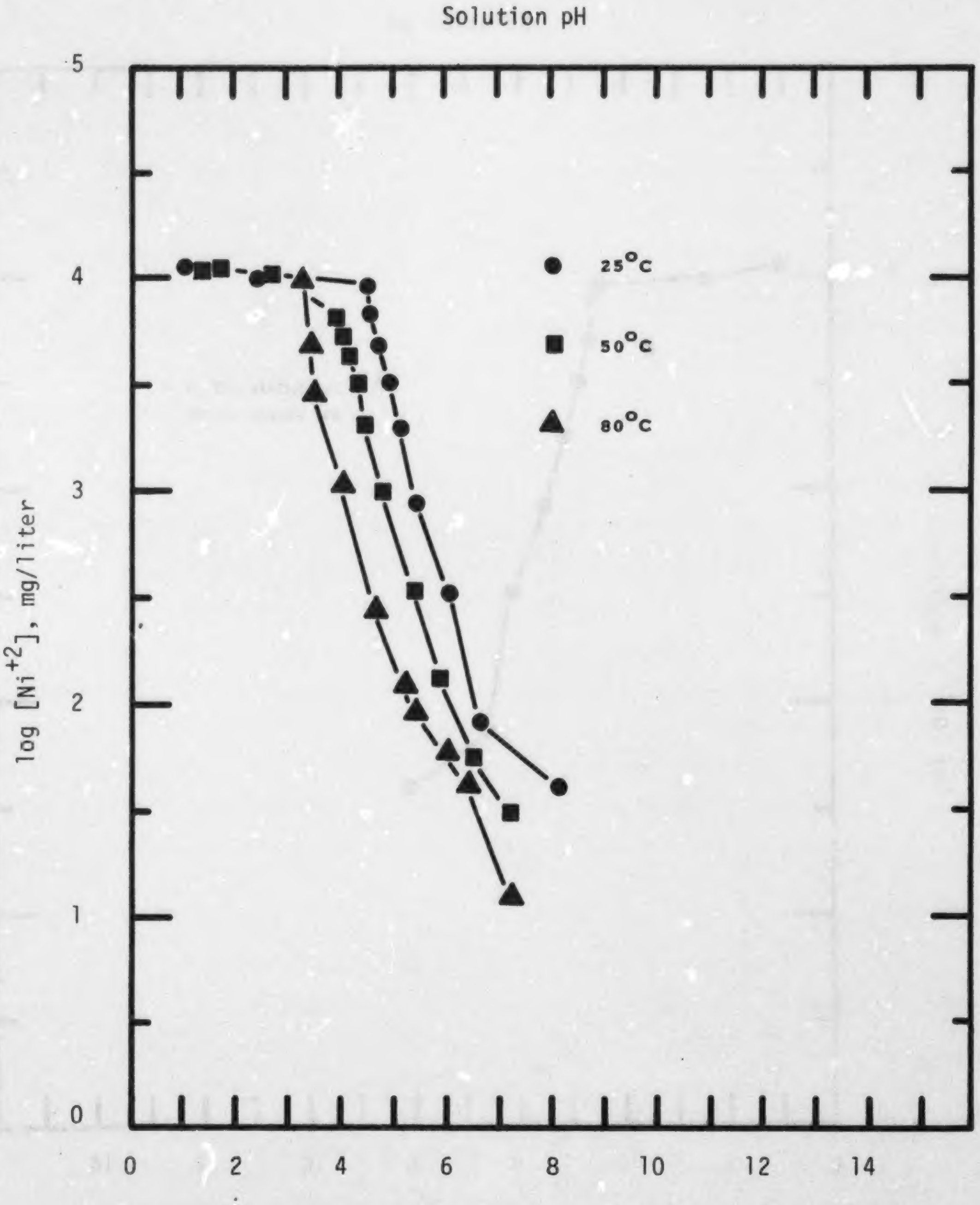

FIGURE 6.29. A COMPARISON OF SOLUBILITY CURVES FOR NICKEL PHOSPHATE PRECIPITATION AT ROOM TEMPERATURE, 50°C, 80°C

Although filterability data were not collected, it was observed that qualitatively the filterability was good.

6.1.1.3.4. Separation of Mixed Metals

6.1.1.3.4.1. Iron-Chromium-Nickel Separation

Once experimental solubilities of pure Fe, Cr and Ni phosphates were established, flowsheet development and testing were initiated. The synthetic solution was prepared by dissolving 40.49g $NiCl_2 \cdot 6H_2O$, 29.03g $FeCl_3$, and 77.31g $Cr(NO_3)_3 \cdot 9H_2O$ in a one-liter solution containing twice the stoichiometric requirement of phosphate for ferric phosphate formation. The initial concentrations of iron, chromium and nickel were each 10 gpl.

The planned procedure was to titrate this solution with two normal NaOH to a pH of 2.0; filter out the iron phosphate; raise the temperature to 50°C, add an additional $1XPO_4$ for chromium precipitation; again titrate with two normal NaOH to a pH of 3.5-4; and solid-liquid separate the solids; and produce a $CrPO_4$ solid and a nickel solution. By raising the solution pH to 7 with two normal NaOH, a nickel phosphate solid could be produced. During the actual test, the planned procedure was varied only by obtaining a sample about every 0.25 to 0.5 pH units.

Iron-Chromium Separation

The iron-chromium precipitation plan worked exactly as was expected. When the slurry was solid-liquid separated at pH = 2.0, the iron concentration had been lowered to 22 mg/liter, meaning 99.76% of the iron originally dissolved had been precipitated. At the same time, the only change in the Cr and Ni concentrations was due solely to dilution with two normal NaOH (283 ml) added in order to raise the pH. The chromium content of the iron product was only 1.2% and the nickel content was only 0.4%. Both these impurities may be present because of solution entrapment.

Chromium-Nickel Separation

The chromium-nickel separation stage of this test did not appear to work as smoothly as the Fe-Cr separation step did. (Note: The dissolved chromium concentration indicated that nearly all the starting chromium dissolved; however, the nickel concentation was about 1.5 (approximately 30%) grams lower than expected) (Figure 6.30). The pH of this test was too high. A better pH would have been 3.0-3.5.

Despite the difficulty in the chromium precipitation stage, the nickel precipitation stage went very well, lowering the nickel concentration to 40 mg/liter by pH 7.8.

From these test data one can now predict a better pH to conduct the chromium-nickel separation stage. If the concentration versus pH graph is studied (Figure 6.30), it can be seen that at pH 3.5 there is less than 100 mg/liter chromium still dissolved, but approximately nine gpl Ni should still be dissolved. At this point of the test, there should only be 5-7 gpl nickel still in solution; thus, if the chromium-nickel separation were conducted at a pH between 3.5 to 3.8, a pure chromium phosphate solid would be expected as well as a virtually chromium-free solution for the nickel precipitation stage. (Note: 100 mg/liter Cr precipitated with the $Ni_2(PO_4)_3$ solid would account for only one to two percent of the nickel solid.)

Another variation which could be made is to perform the chromium-nickel separation at 80°C, because both chromium and nickel phosphate precipitation are temperature-dependent. Even though nickel is not as dependent on temperature as is chromium, pH would have to be well-controlled, as is the case at 50°C. Due to the increased evaporation rates for H_2O at 80°C over 50°C, control would be very difficult. There does not appear to be a great advantage to precipitating chromium at 80°C.

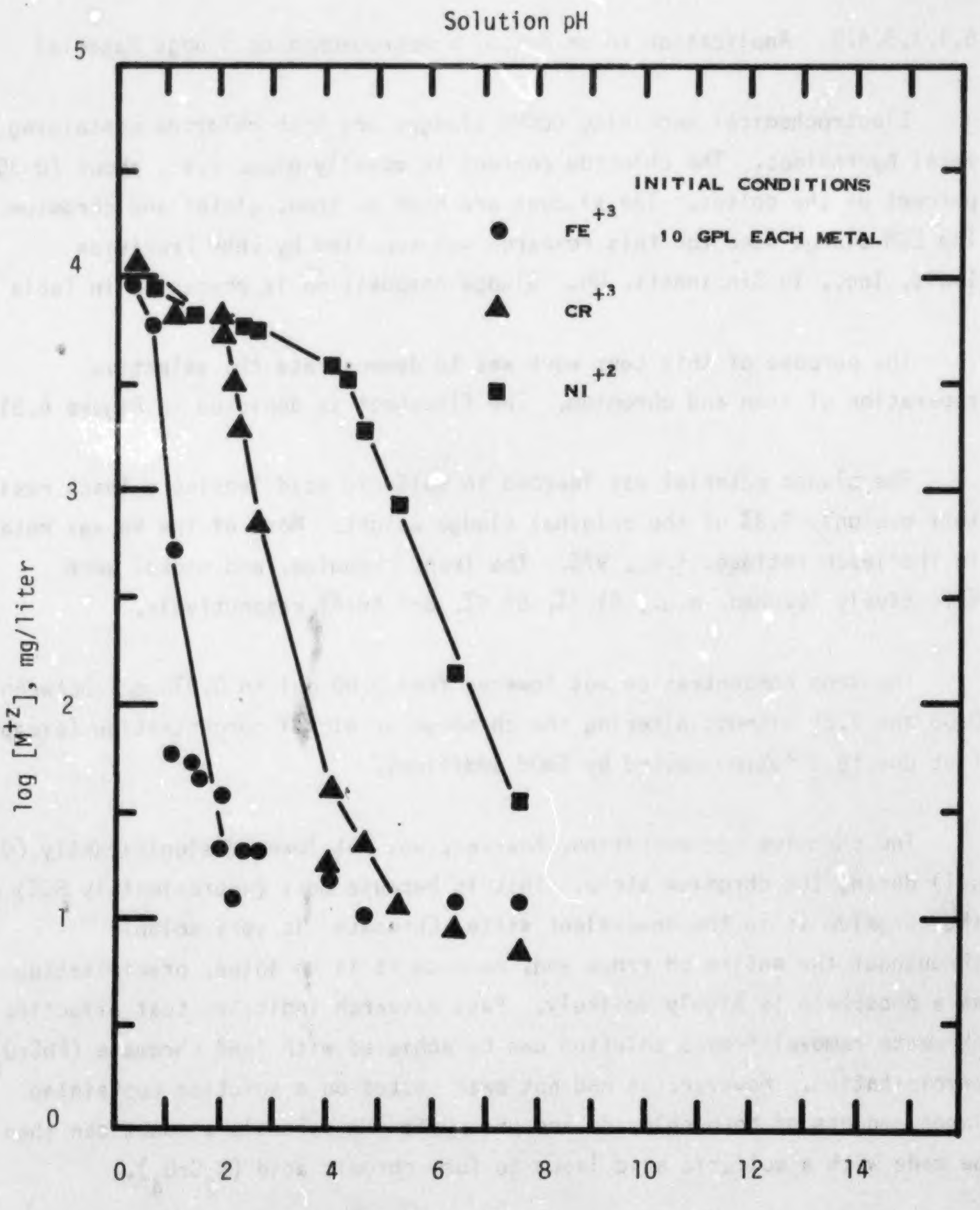

FIGURE 6.30. SOLUBILITY CURVE FOR IRON PRECIPITATION AT ROOM TEMPERATURE, CHROMIUM PRECIPITATION AT 50°C, AND NICKEL PRECIPITATION AT 50°C DURING THE MIXED METAL TEST

6.1.1.3.4.2. Application to an Actual Electromachining Sludge Material

Electrochemical machining (ECM) sludges are high chloride containing metal hydroxides. The chloride content is usually high, i.e., about 20-30 percent of the solids. The sludges are high in iron, nickel and chromium. The ECM sludge used for this research was supplied by Lehr Precision Tools, Inc., in Cincinnati, OH. Sludge composition is presented in Table 6.6.

The purpose of this test work was to demonstrate the selective separation of iron and chromium. The flowsheet is depicted in Figure 6.31.

The sludge material was leached in sulfuric acid leaving a leach residue that was only 9.3% of the original sludge weight. Most of the Nb was retained in the leach residue, i.e., 97%. The iron, chromium, and nickel were effectively leached, e.g., 81.3%, 89.4%, and 88.6% respectively.

The iron concentration was lowered from 3.66 gpl to 0.038 gpl between pH 0.88 and 2.29 without altering the chromium or nickel concentration (except that due to dilution caused by NaOH addition).

The chromium concentration, however, was not lowered significantly (0.11 gpl) during the chromium strip. This is because most (approximately 80%) of the chromium is in the hexavalent state. Chromate is very soluble throughout the entire pH range and, because it is an anion, precipitation as a phosphate is highly unlikely. Past research indicates that effective chromate removal from a solution can be achieved with lead chromate ($PbCrO_4$) precipitation. However, it had not been tested on a solution containing large amounts of both chloride and phosphate. A saleable product can then be made with a sulfuric acid leach to form chromic acid (H_2CrO_4).

Quantitative digestion results also support the earlier claim that little or no chromium or nickel precipitated with the ferric phosphate (Table 6.7). Likewise, the chromium phosphate was also very low in contaminants, even though the solids were not washed (Table 6.8).

TABLE 6.6. ECM SLUDGE COMPOSITION

Element	Composition, %
Fe	5.7
Cr	3.8
Ni	16.6
Na	23.8
Cl	9.0
Nb	1.8

Note: Composition determined by SEM-EDAX

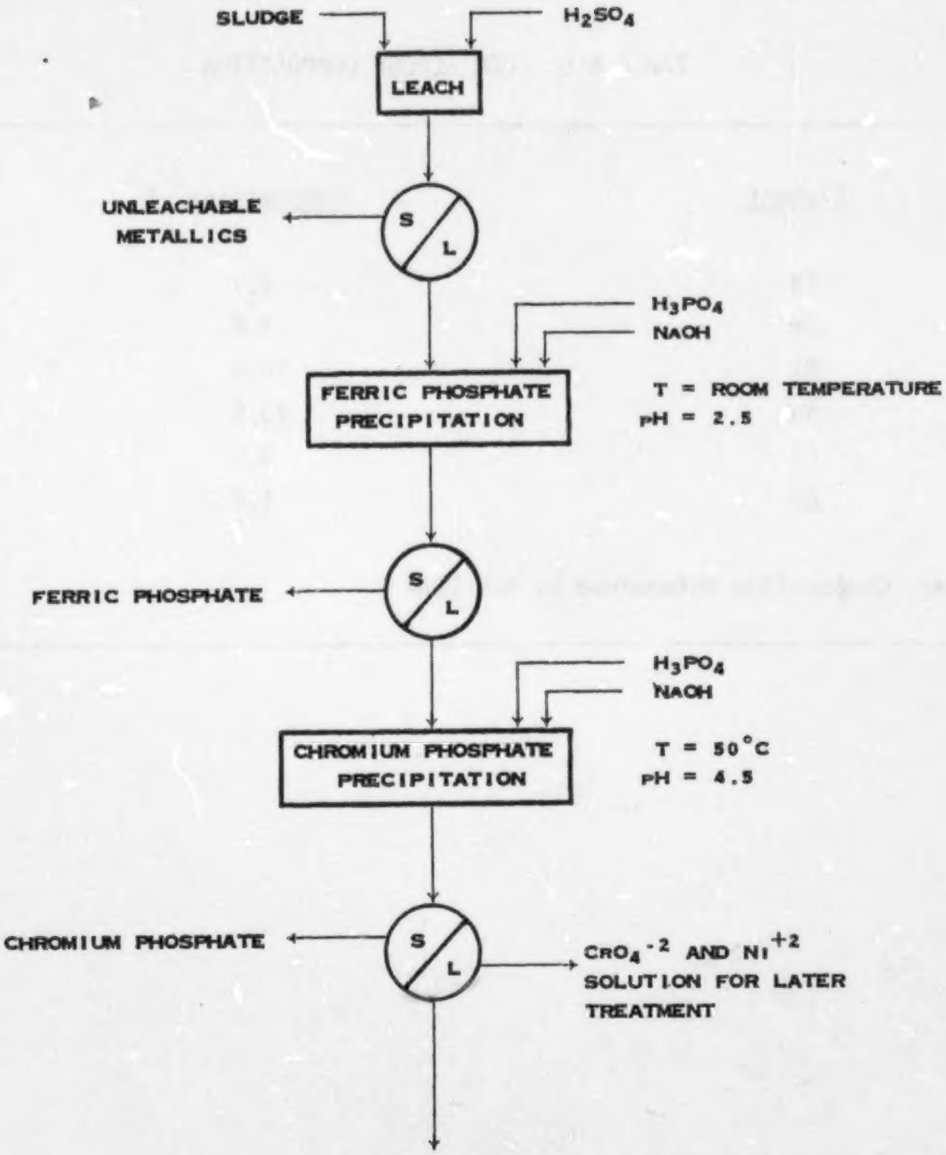
SLUDGE
H_2SO_4
LEACH
UNLEACHABLE METALLICS
S
L
H_3PO_4
NAOH
FERRIC PHOSPHATE PRECIPITATION
T = ROOM TEMPERATURE
pH = 2.5
FERRIC PHOSPHATE
S
L
H_3PO_4
NAOH
CHROMIUM PHOSPHATE PRECIPITATION
T = 50°C
pH = 4.5
CHROMIUM PHOSPHATE
S
L
CrO_4^{-2} AND Ni^{+2} SOLUTION FOR LATER TREATMENT

FIGURE 6.31. FLOWSHEET FOR IRON AND CHROMIUM REMOVAL FROM LEHR SLUDGE

TABLE 6.7 QUANTITATIVE DIGESTION DATA FOR FERRIC PHOSPHATE SOLIDS PRODUCED FROM LEHR SLUDGE TREATMENT (Test 18)

Solids Treated, g	Element Content, %		
	Fe	Cr	Ni
0.108	23.16	U.D.	U.D.
0.118	25.27	U.D.	U.D.
0.106	25.61	U.D.	U.D.

Note: U.D. = undetectable by ICP, < 0.05 mg/liter.

TABLE 6.8 QUANTITATIVE DIGESTION DATA FOR CHROMIUM PHOSPHATE SOLIDS PRODUCED FROM LEHR SLUDGE TREATMENT

Solids Treated, g	Element Content, %		
	Fe	Cr	Ni
0.098	2.44	14.51	1.13
0.118	2.03	14.54	1.17
0.100	2.15	14.48	1.10

The following conclusions were made from this test work:

- Ferric phosphate can be effectively precipitated from ECM sludge without any contamination or hinderance from Cr^{+3} and Ni^{+2};

- Most of the chromium present is in the (+6) form;

- Chromium(+3) can be recovered from solution without contamination from nickel;

- Most of the refractory metals contained in the alloy (Nb, Mo, Ti, etc.) will not leach but will probably be lost, unless they are separated prior to ferric phosphate precipitation.

After completing the above test work it was obvious that the original flowsheet needed to be modified so that chromium (VI) could be recovered. During a previous EPA-sponsored research project (1), pilot plant tests were conducted at Montana Tech to remove chromate from solution as $PbCrO_4$. The $PbCrO_4$ was then redissolved with sulfuric acid to produce chromic acid:

$$PbCrO_4(s) + H_2SO_4 = PbSO_4(s) + H_2CrO_4$$

Therefore, a technically-proven process to remove chromate from solution was available. During this study, $PbCrO_4$ was tested as a means of removing chromate from an ECM sludge leach solution after iron and chromium (III) removal was complete. Cobalt was also added to this leach. This was done because there was also a great deal of interest in cobalt-nickel separations. However, the cobalt results will not be discussed.

6.1.1.3.4.2.1. Procedure for Test Work

The procedure used during this test work is listed below:

- One-half liter of leach solution was prepared from Lehr sludge material.

- The solution was sparged with chlorine gas to insure all the chromium was oxidized to chromate.
- The pH was raised to 4.5.
- The solids were filtered from the solution (the solids should be Co_2O_3, and $FePO_4 \cdot 2H_2O$).
- The filtrate was split into two solutions.
- To one solution $PbNO_3$ was added, and the pH was maintained at 4-5 (Test 19C).
- The solids were collected and characterized.
- The filtrate was analyzed for chromium.
- The pH of the filtrate was raised to nine to precipitate $Ni(OH)_2$.
- The other solution was treated by raising the pH to eight (Test 19B).
- Solids were filtered (the solids should be $Ni(PO_4)_2$ and $Ni(OH)_2$).
- Lead nitrate was added and the pH was adjusted to 4-5.
- Solids were separated ($PbCrO_4$) and the filtrate analyzed.

The iron and cobalt were effectively stripped from solution by phosphate precipitation at a pH of 4.5, e.g., the iron content was lowered from 2.6 gpl to 0.013 mg/liter; the cobalt was lowered from 1.7 gpl to 0.026 mg/liter. The chromium content of the starting solution was 2.1 gpl, and the nickel content was 6.3 gpl.

6.1.1.3.4.2.2. Recovery of Nickel Prior to Chromium (Test 19B)

Test 19B was a test designed to study the precipitation of $Ni_3(PO_4)_2$ and $Ni(OH)_2$ before precipitating $PbCrO_4$.

To precipitate $Ni_3(PO_4)_2$ and $Ni(OH)_2$ 11.5 ml of five normal NaOH was added to the solution. A precipitate formed immediately, and the pH rose quickly to 12.0. ICP analysis indicated that the nickel concentration was now less than 0.05 mg/liter. The chromium concentration, as was expected, remained unchanged except for dilution at 1.59 gpl.

After solid/liquid separation, the filtrate was saved for the $PbCrO_4$ precipitation step. Lead was introduced to the solution as $Pb(NO_3)_2$. In order to insure enough lead, two times the stoichiometric amount was added to the solution. Upon adding $Pb(NO_3)_2$ a yellowish white precipitate immediately formed, and the pH dropped to 8.8 from 12.0. However, because the filtrate remained yellow 1.5 hours after the lead addition, 1X Pb was again added to the slurry. The pH dropped to 6.1, and the filtrate became clear. ICP data for the final concentrations of metals are presented in Table 6.9.

6.1.1.3.4.2.4. Recovery of Chromium Prior to Nickel (Test 19C)

The test for 19C required that enough lead nitrate be added to complete the formation of $Pb_5(PO_4)_3Cl$ because of the excess phosphate and chloride contained in this solution. This meant 6.45 grams had to be added for a volume of approximately 0.30 liters.

TABLE 6.9. RESULTS FOR TESTS ON RECOVERY OF NI PRIOR TO CR

	Element Considered					
	Fe	Cr	Ni	Co	Pb	Na
Nickel Precipitation						
Amount Precipitated, %	–	10	100	–	–	–
Amount Remaining in Solution, %	–	90	–	–	–	–
Lead Chromate Precipitation, pH =8.0						
Amount Precipitated, %	–	64.5	–	–	100	–
Amount Remaining in Solution, %	–	33.5	–	–	–	–
Lead Chromate Precipitation, pH=6.1						
Amount Precipitated, %	–	100	–	–	99.8	–
Amount Remaining in Solution, %	–	–	–	–	0.2	–

After completion, the lead and chromium concentrations were both extremely low (68 mg/liter Pb and 19 mg/liter Cr), and the remaining solution still contained a substantial amount (6.23 gpl) of nickel as evidenced by a bright yellow precipitate and green filtrate.

Once the chromate recovery was complete, the next step was precipitation of nickel hydroxide. This was accomplished by raising the pH to 8.4 with one normal NaOH. Results are presented in Table 6.10.

6.1.1.3.4.2.4. Conclusions

The main conclusions from Test 19 are as follows:

- All phosphate should be removed from solution prior to $PbCrO_4$ precipitation. If phosphate and chloride are present $Pb_5(PO_4)_3Cl$ will form in preference to $PbCrO_4$ and consume a great deal of lead in a relatively useless compound.

- $PbCrO_4$ and $Ni_3(PO_4)_2$-$Ni(OH)_2$ precipitation can produce pure solids for potential markets, and produce a discharge water which contains little, if any, dissolved metals.

6.1.1.4. Separation of Iron, Chromium, Nickel, and Zinc from Aqueous Ammonia Solutions

The results of this study are presently being summarized and will be available in a thesis presentation (10) by December, 1987. The general conclusion at this time is that gaseous ammonia can be used as the neutralizing agent in place of caustic without influencing the separability of iron and/or chromium from aqueous divalent cations.

TABLE 6.10. MASS BALANCE FOR TESTS ON REMOVAL OF Cr PRIOR TO Ni

	Element Considered		
	Pb	Cr	Ni
Lead Chromate Precipitation,			
Amount Precipitated, %	99.5	98.99	3.1
Amount Remaining in Solution, %	0.5	0.01	96.9
Nickel Precipitation			
Amount Precipitated, %	–	–	94.4
Amount Remaining in Solution, %	–	–	5.6

6.1.1.5. Conversion of Ferric Phosphate to Ferric Hydroxide

Nordwick (11) investigated the conversion of ferric phosphate to ferric hydroxide. This conversion is very important because there is not a very large market for ferric phosphate. By converting ferric phosphate to ferric hydroxide, a disposable solid is produced and phosphate reagent is regenerated for recycle. Reagent recycle, of course, improves the economics of the process.

An important feature of the phosphate process is the ability to convert the trivalent phosphate to a disposable product while regenerating the phosphate reagent for reuse and/or the conversion of metal phosphates to a commercially useful product. The solution condition necessary to convert ferric phosphate to ferric hydroxide is predicted in Figure 6.32, e.g., thermodynamically, ferric phosphate should be converted to ferric hydroxide at a pH of approximately 3. However, in actual practice more severe conditions are required to successfully accomplish the conversion.

A series of kinetic studies have been performed to evaluate the rate of conversion of ferric phosphate to ferric hydroxide :

$$FePO_4 \cdot 2H_2O(s) + H_2O = Fe(OH)_3(s) + HPO_4^{=} + 2H^+$$

The rate of reaction was followed by exposing a slurry of ferric phosphate to a pH-controlled water environment, and by measuring the phosphate concentration in the solution as a function of time. A portion of the results of the study are presented in Figure 6.33. The best conversion was achieved at pH = 12, 50°C. The kinetics of the conversion process follow the product layer shrinking model, Figure 6.34.

The influence of several variables on the conversion process, e.g., time, temperature, pH, solids content, agitation rate, phosphate concentration, inert solids, and the presence of humic acid, has been investigated and the results are summarized in Table 6.11. The test results presented in Table

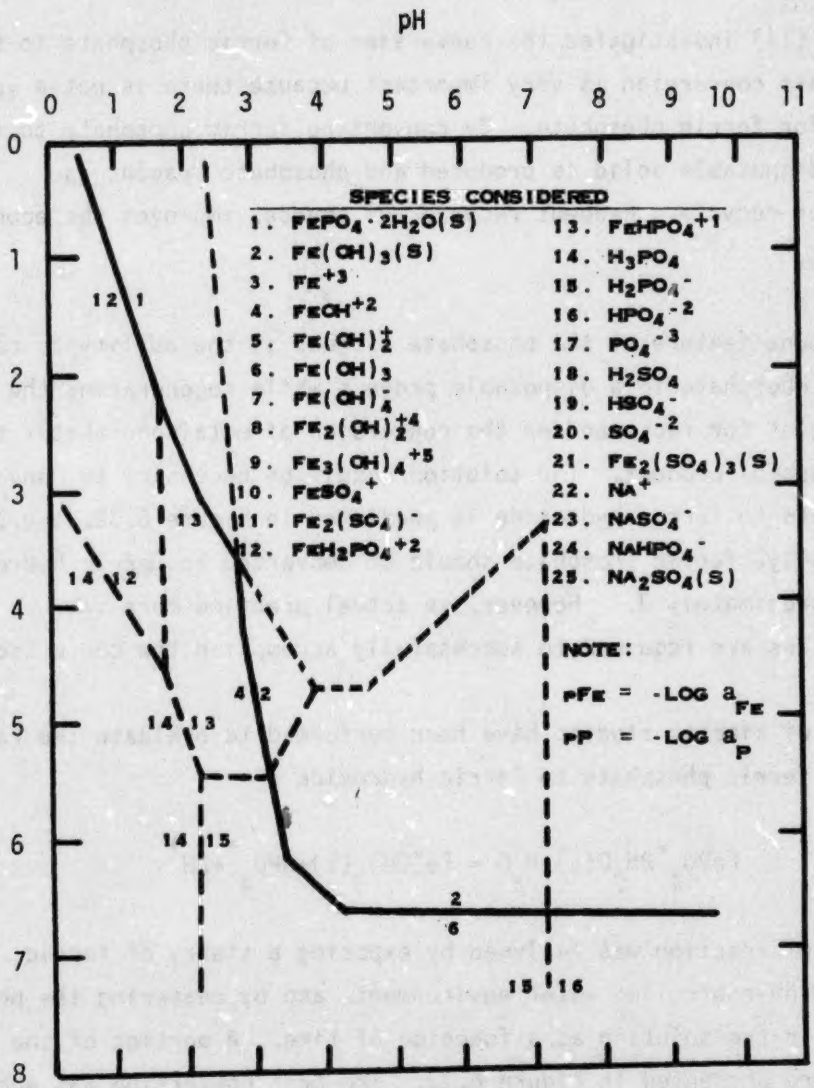

FIGURE 6.32. FERRIC PHOSPHATE STABILITY DIAGRAM FOR THE FERRIC-PHOSPHATE-SULFATE-WATER SYSTEM

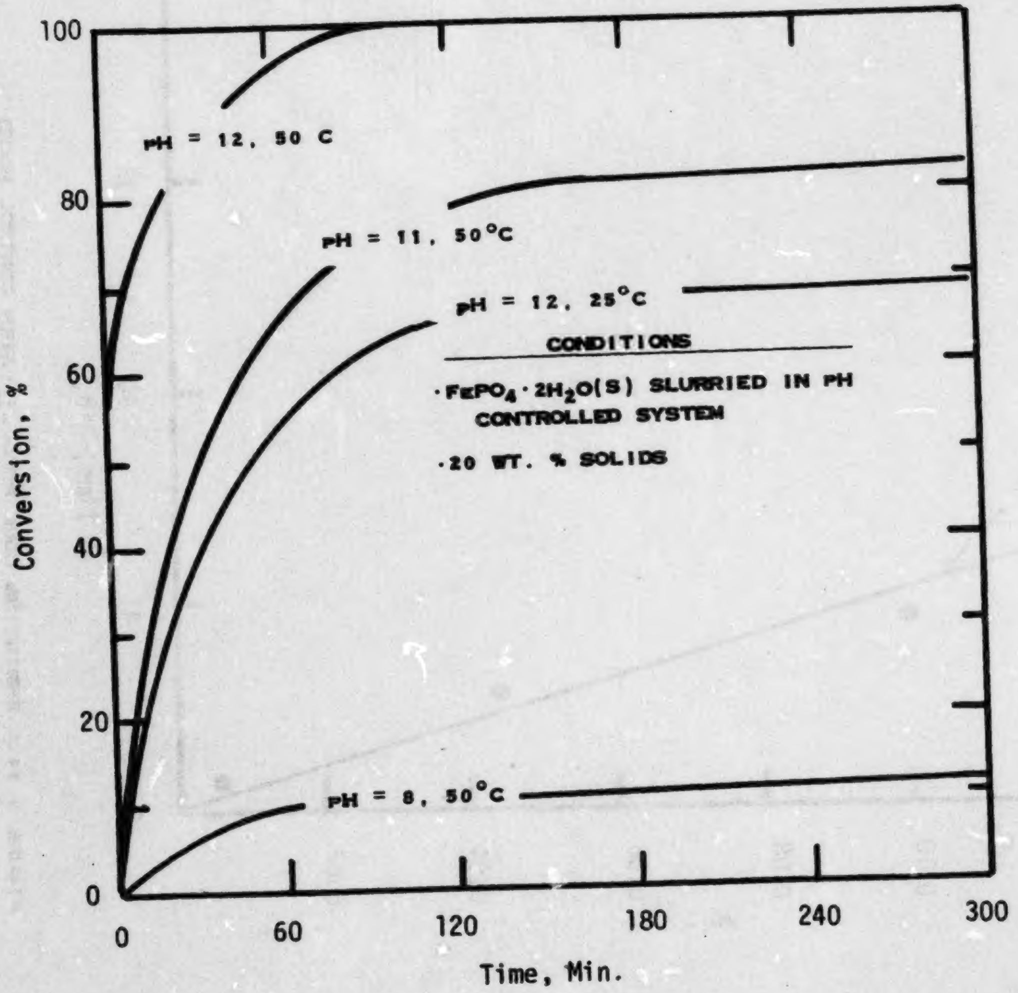

FIGURE 6.33. THE RATE OF CONVERSION OF FERRIC PHOSPHATE TO FERRIC HYDROXIDE AS A FUNCTION OF PH AND TEMPERATURE

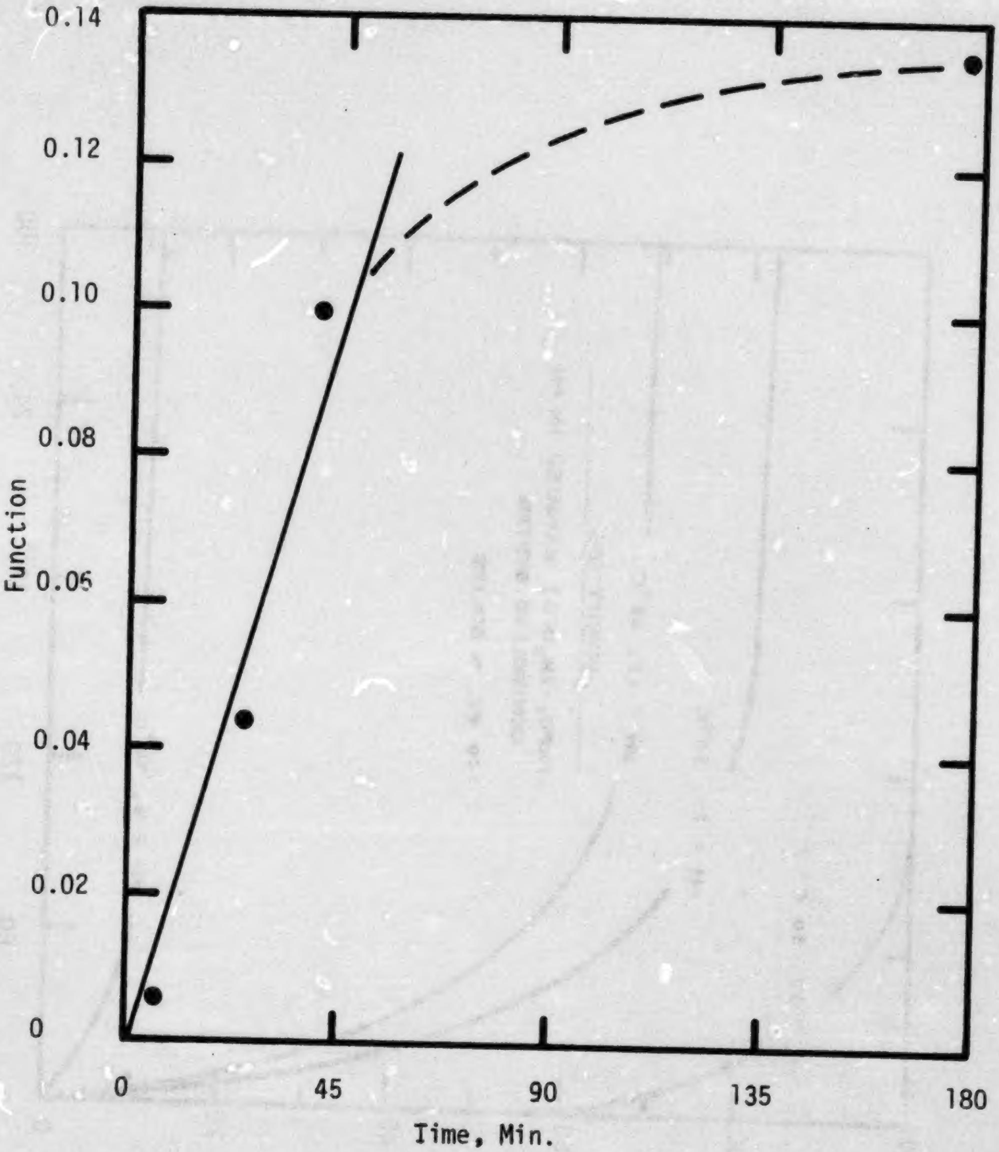

FIGURE 6.34. SHRINKING CORE PRODUCT LAYER CONTROL MODEL

TABLE 6.11. CONVERSION TEST RESULTS AT PH = 11, 50^0C

Conditions	Converted from P analysis (%)	Converted from solid analysis (%)	Total Test Time (Min.)	Filterability (10^{10} g/cm)	Volume 1N NaOH (ml)
20% Solids	85.0	68.2	120	5.224	593
40% Solids	89.6	71.7	90	3.125	593
Undried Solids	81.7	70.6	120	31.310	523
Excess PO_4^{-3}	79.8	72.9	120	22.340	857
Amorphic Solids	63.5	78.7	90	31.440	673
Using Humic Acid	82.7	62.8	120	17.780	536
At High Mixing	95.0	86.4	90	------	979
With 20% Silica	81.3	89.8	40	------	1258

6.11 that show excellent conversions are possible. The filterability (also shown in Table 6.11, of the converted solids is certainly less than ferric phosphate but the rates are acceptable.

The conditions necessary for good conversion appear to be acceptable for commercial use, i.e., approximately 50°C, two-hour residence time at 20-40 weight percent solids in a moderately agitated reactor.

6.1.1.6. Conversion of Chromium Phosphate to Marketable Chromium Products

Chromium phosphate precipitation is an effective way to remove trivalent chromium from divalent cations in an acid solution. Its marketability is, however, limited. Quinn (13) is presently completing an experimental investigation to study the conversion of chromium phosphate to more valuable and more marketable chromium products.

Nordwick (11) previously investigated the conversion of chromium phosphate to chromium hydroxide by controlling the solution pH at values above eight. The results were not favorable, i.e., less than ten percent conversion was achieved at pH levels up to 12 at temperatures up to 50°C. Quinn has taken a different approach. He has investigated the conversion by soda ash fusion.

The experimental procedure consists of roasting the chromium phosphate with sodium carbonate in air to form sodium chromate which is subsequently leached with water to solubilize the chromium as chromate. The chromate solution also contains most of the phosphorus present in the original solid as phosphate ions. This needs to be removed before further processing of the leach solution. The phosphate can be removed by adding ferric iron in slight excess to the soichiometric requirement for complete phosphate removal. Because chromate is soluble at all pH values, it will not be precipitated but ferric phosphate will cleanse the solution of phosphate and the excess iron will precipitate as ferric hydroxide. These solids can be separated from solution, leaving a relatively pure sodium chromate solution. The chromate can be recovered by precipitation as lead chromate (pH = 3-4); thoroughly rejecting sodium. The lead chromate can be redissolved in sulfuric acid to form lead sulfate solid (which can be recycled to the chromate precipitation unit operation) and chromic acid.

The anticipated flowsheet is presented in Figure 6.35. As shown in the flowsheet, the initial treatment step will be a sodium carbonate fusion operation. The chromium phosphate is mixed with sodium carbonate then fused for one hour at about 720°C. The fusion product is then crushed and screened to - 60 mesh. This operation provides small particles that provide good surface availability for the subsequent leach operation. Following screening the fusion product is leached with water for one hour. The natural pH of this leach solution ranges from about 10.5 - 12.0. A simple solid/liquid separation is then performed. The majority of the contaminants report to the solid phase while greater than 90% of the chromium reports to the liquid phase.

The chromium phosphate used for the current test work was a mixture of chromium phosphate materials produced in two of the large scale tests. The composition of the starting composited material is presented in Table 6.12.

A Plackett Burkman variables design matrix study was performed on the fusion process to determine which variables had a significant affect on the chromium recovery during fusion. The four variable that were tested included: fusion time (high: 1 hr, low: 2 hr), temperature (high: 700°C, low: 500°C), charge mixing (high: fusion charge removed from furnace and stirred every 15 minutes, low: no mixing of charge), sodium carbonate/chromium phosphate ratio (high: 2.5, low: 1.0).

Test results from the Plackett Burhman design matrix test showed that the only significant variable affecting the fusion operation was the temperature at which the fusion was performed. It should be noted that the number chosen for the population value was based on a desired confidence level of 99%. Variables other than temperature demonstrate a significant effect on fusion only if one reduces the confidence level to 90% or lower.

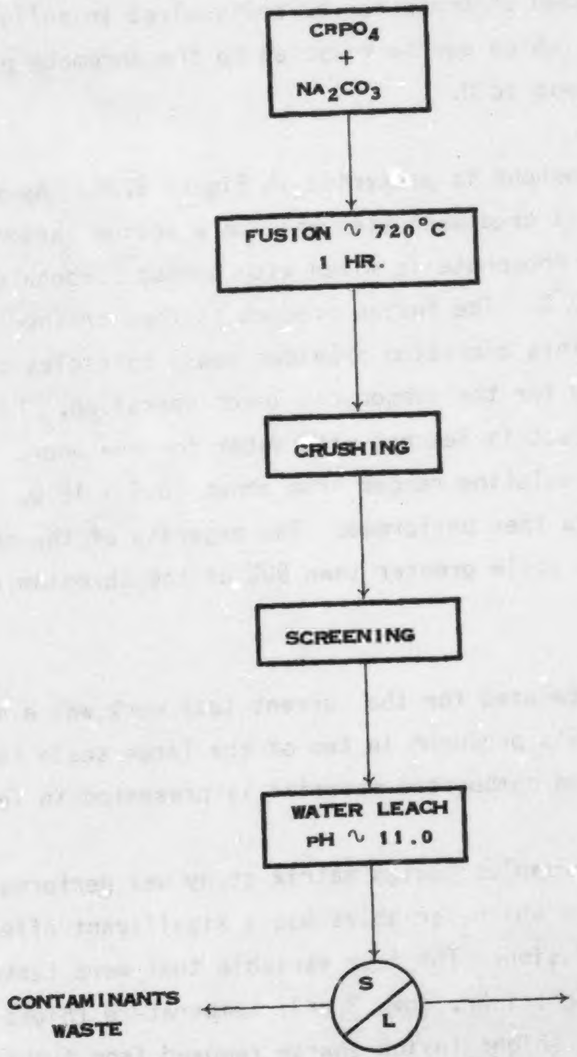
CRPO4
+
NA2CO3
FUSION ∿ 720°C
1 HR.
CRUSHING
SCREENING
WATER LEACH
pH ∿ 11.0
S
L
CONTAMINANTS
WASTE
CHROME
VALUE

FIGURE 6.35. CHROMIUM PHOSPHATE CONVERSION BY SODIUM CARBONATE FUSION

TABLE 6 12. COMPOSITION OF COMPOSITED CHROMIUM PHOSPHATE

Element	Composition, %
Fe	0.83
Cr	21.68
Ni	1.48
Zn	0.82
Al	3.20
Ca	0.46
Si	0.02
P	11.70

TABLE 6.13. RECOVERY OF ELEMENTS FROM FUSION PRODUCTS

Condition			Recovery, %					
T°C	Time,Hr	Charge Ratio	Fe	Cr	Ni	Zn	Al	P
718	1	1/2.5	1.0	90.6	8.9	3.0	50.3	106.9
718	1	1/2.5	-	91.8	7.8	1.6	44.8	101.6
709	1	1/1	2.8	70.0	49.3	5.6	38.1	68.4
709	1	1/1	-	80.2	47.9	5.5	11.8	55.1

Note: Recovery calculated from analyses of fusion solid and filtrate.
Charge ratio: chromium phosphate/sodium carbonate.

Although the Plackett Burhman results show that temperature is the only significant variable, literature indicates all four variables should influence the recovery. Therefore, a series of tests were performed using the other variables. The results are reported in Table 6.13. It should be noted that these recoveries are calculated based on the analysis of the fusion charge recovered and the analysis of the filtrate.

Fusion operation conditions that provide for optimium chromium recovery appear to be: roasting at 720 ^{o}C for one hour at a chromium phosphate/sodium carbonate ratio of 1/2.5. The leaching of the fusion product formed under these conditions results in greater than 92% of the chromium reporting to the filtrate. Also, only 1.6% of the zinc and 7.8% of the nickel report to the filtrate under these fusion conditions. The only possible problem may be that nearly half, 44.8% of the aluminum reports to the filtrate under these conditions.

The fusion operation has been optimized. Further work on the leaching unit operation will further enhance the chromium recovery and impurity rejection in the filtrate. Work will be performed to optimize and formulate a standard leach procedure with specific leach conditions of pH, time, temperature, and fusion solid to water ratio.

6.1.1.7. Rate of Chromium Removal from Acidic Aqueous Sludge Leach Solutions

McGrath (14) is presently investigating the rate at which chromium is precipitated from phosphate bearing chromium aqueous solutions. The following is a progress report on this work. The final results will be available in thesis form by December, 1987.

6.1.1.7.1. Introduction

Since the separation of ferric and chromic ions by precipitating the respective phosphates at different temperatures is a direct result of the unique stability of chromium (+3) ion and its various complexes in aqueous solutions, a brief review of the fundamental chemistry of this ion is helpful in interpreting the phenomena associated with chromium phosphate precipitation. In solution the chromic ion invariably is present in the octahedral co-ordination with six nearest neighbor atoms of some ligand system. If all six ligands are H_2O, the ion exists as trivalent $Cr(H_2O)_6$, the hexa aquo chromium ion. Energetically this configuration is much more stable than the free ion since the degeneracy of the d-orbitals which exist in the free ion is removed under the influence of the octahedral ligand field. The five d-orbitals are split into two groups: a t_{2g} set of three orbitals which is lowered in energy, and an e_g set of two orbitals raised in energy. Now, Cr(+3) has a total of three d electrons which occupy the stabilized t_{2g} set of orbitals, spins parallel according to Hund's Rule. This stabilization energy is expressed in terms of a quantity Δ, the energy difference involved in the d-orbital splitting.

The configuration in which three electrons occupy the t_{2g} set of orbitals with parallel spins is extremely stable because no electron pairing energy is subtracted from the stabilization energy gained from the ligand field splitting. The magnitude of the splitting can be determined from the absorption spectrum of a complex. The stabilization energy amounts to about 59 kcal/mole for the hexa aquo ion (26). This stability confers an inertness upon Cr(+3) complexes, as reflected in the relative second order rate constants observed for water exchange among various metal ions shown in Table 6.14. Xu et.al.(27) measured the rate of water exchange using oxygen 18 as a tracer. Their data indicate that the mechanism for water exchange can be described as an associative interchange, to use their terminology. This means that the geometry of the transition state is one in which an addditional water molecule must be accomodated within the primary solvation shell, something resembling a pentagonal bipyramid. The stabilization energy obtained from the octahedral arrangement of ligands must be at least partially overcome for the atoms in the complex to adopt the requisite transition state geometry. These authors measured the enthalpy of activation as 29 kcal/mole for the exchange process.

TABLE 6.14. CHARACTERISTIC SECOND ORDER RATE CONSTANTS FOR WATER EXCHANGE IN THE PRIMARY SOLVATION SHELL OF METAL IONS

Ion	K_w, moles/sec
Cr^{+3}	3.6 E-5
Mn^{+2}	3.4 E+6
Fe^{+3}	3.3 E+2
Co^{+3}	<1 E+2
Co^{+2}	1.2 E+5
Ni^{+2}	2.9 E+3
Cu^{+2}	>9 E+8
Zn^{+2}	5 E+6
Cd^{+2}	9 E+7
Hg^{+2}	4 E+8

Note: Data from reference 28.

In brief, the stability of the chromic ion in an octahedral ligand field make the attainment of the transition state geometry more difficult, and reactions involving ligand exchange occur more slowly for Cr(+3) than for other metal ions.

Another important aspect of Cr(+3) chemistry is the tendency towards hydrolysis and oligomerization. The hexa aqua chromium ion is not a particularly strong acid (pKa=4.1) (29), but the higher oligomers are strong acids. Although the structural chemistry of these oligomers remains controversial (30), the last decade has seen much progress toward isolating and characterizing individual polymeric species as well as determining equilibrium relationships between them (31-34). Shown in Table 6.15 are some properties of the various oligomers and a value for the free energy of formation at 298 K calculated from the authors' data.

Using these recent data it is possible to construct species distribution and stability diagrams of the chromium-water system. These diagrams are of great utility in characterizing the leach solutions prior to the precipitation reaction. For example, the species distribution diagram constructed using data from Table 6.15 predicts the trimer and its conjugate base to be the most stable species over the pH range of 1-6 which is also revealed in the stability diagram of the chromium-water system (Figures 6.36 and 6.37). One of the objectives in this phase of the project is to determine if the chromium speciation prior to precipitation has any affect on the rate of precipitation or the type of precipitate formed. Obviously, the extension of these equilibrium diagrams to higher temperatures will be required since the leach solutions are subjected to high temperatures for a period of time. After the solution cools the chromium speciation is metastably located near the high temperature equilibrium. At 25 degrees hydrolysis equilibria are slow to arrive. In our laboratory one series of experiments that was designed to produce solutions of known specie composition required 13 weeks for equilibrium to be established, Table 6.16.

Additional species that are of interest include the sulfate complex of the mononer (35),and, possibly of the dimer (36). These almost certainly

TABLE 6.15. AQUEOUS CHROMIUM SPECIES AND THEIR PROPERTIES

Specie	Color	pKa	G_f^o, kcal/mole	Reference
$Cr(H_2O)_6^{+3}$	violet	4.1	-51.51	27
$Cr(OH)^{+2}$	blue-vio.	6.1	-102.57	
$Cr(OH)_2^{+}$	blue-vio.	-	-150.94	
$Cr_2(OH)_2^{+4}$	blue-vio.	3.68	-209.66	
$Cr_2(OH)_3^{+3}$	-	-	-261.39	
$Cr_3(OH)_4^{+5}$	green	4.35	-380.65	
$Cr_3(OH)_5^{+4}$	green	5.63	-431.41	
$Cr_4(OH)_6^{+6}$	green	2.55	-526.29	
$Cr_4(OH)_7^{+5}$	green	5.08	-578.17	

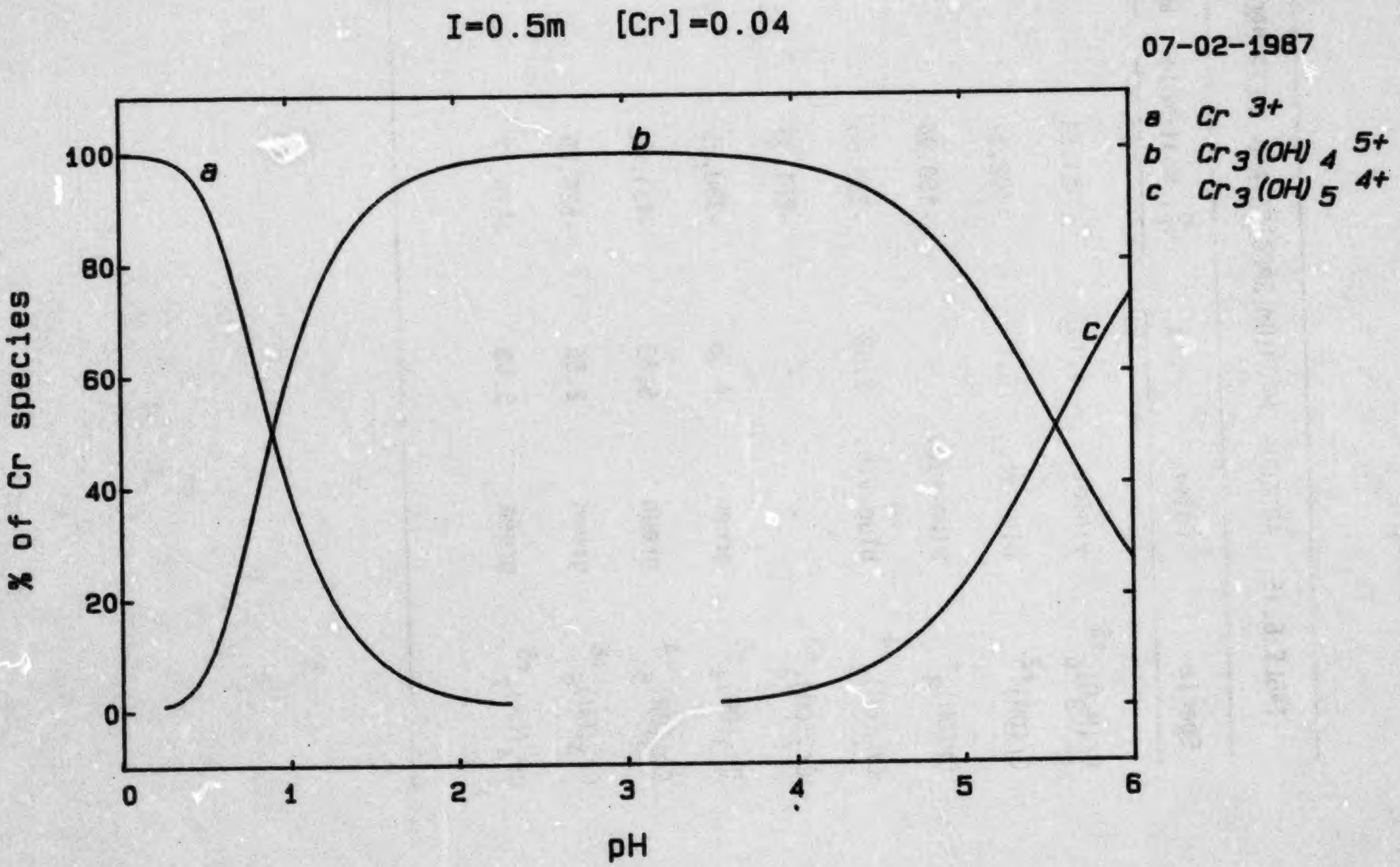

FIGURE 6.36. SPECIES DISTRIBUTION DIAGRAM FOR CHROMIUM

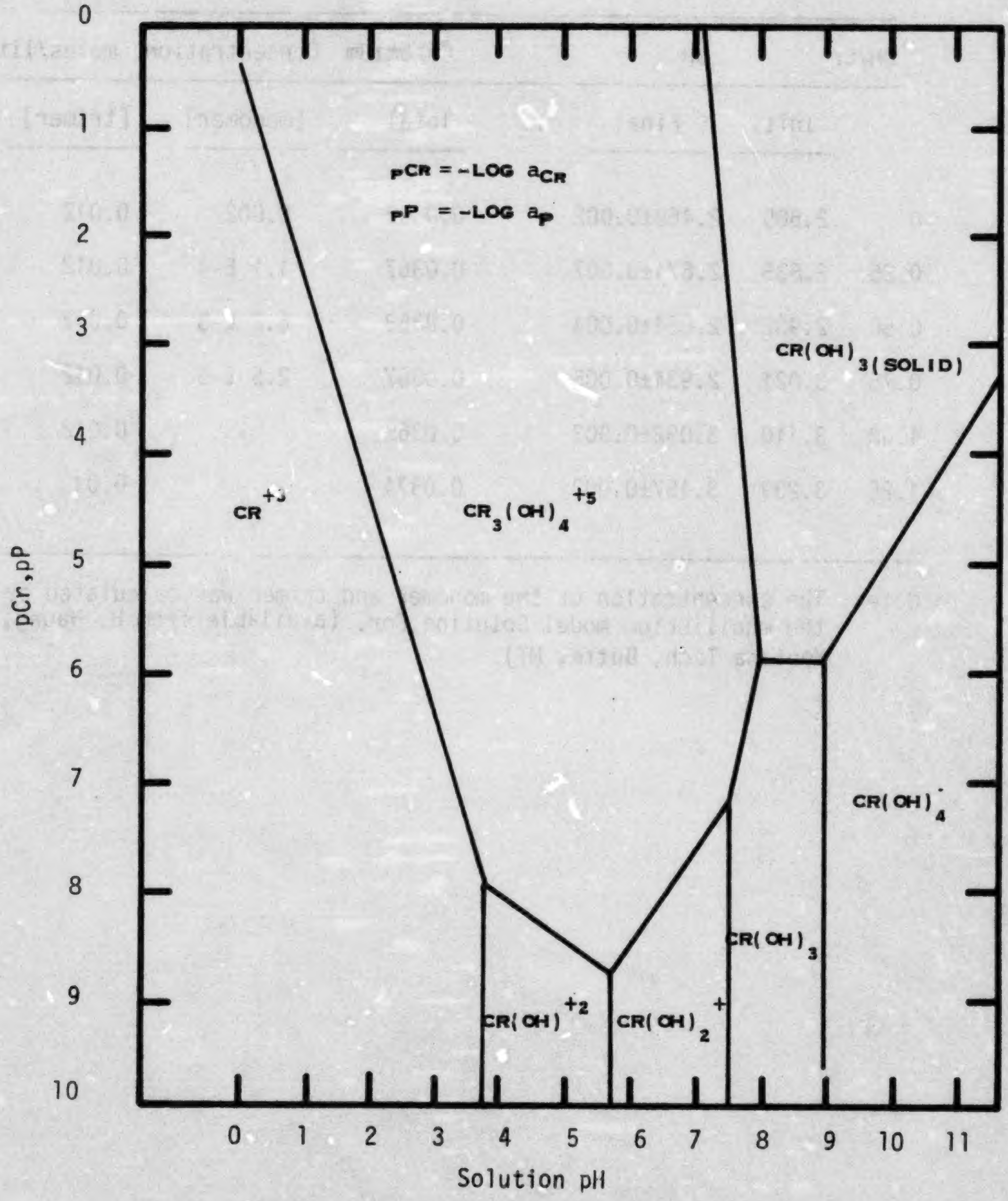

FIGURE 6.37. STABILITY DIAGRAM FOR THE CHROMIUM-WATER SYSTEM

TABLE 6.16. SOLUTIONS OF CONTROLLED Cr SPECIATION
I = 0.5 M

OH/Cr	pH		Chromium Concentration, moles/lit.		
	init.	Final	Total	[monomer]	[trimer]
0	2.605	2.468±0.002	0.0362	0.002	0.012
0.25	2.835	2.671±0.007	0.0367	1.1 E-4	0.012
0.50	2.932	2.854±0.004	0.0363	6.2 E-5	0.012
0.75	3.021	2.934±0.005	0.0367	2.5 E-5	0.012
1.00	3.110	3.092±0.003	0.0369	-	0.012
1.25	3.209	3.157±0.003	0.0374	-	0.012

Note: The concentration of the monomer and trimer was calculated by the equilibrium model Solution.For. (available from H. Haung, Montana Tech, Butte, MT).

exist in the leach solution, and their inclusion in the equilibrium models would be more representative of the leach solution species composition.

6.1.1.7.2. Chromium Phosphate Precipitation

Polymorphism of solid chromium phosphates has long been recognized (37). Depending on the temperature, a variety of compounds can be precipitated. At low temperatures a violet hexahydrate ($CrPO_4.6H_2O$) is formed (38). Two other polymorphs of the crystalline form exist (and), but the form is extremely unstable. At temperatures slightly above room temperature, a green amorphous solid is produced with varying numbers of hydration waters (37,38). This agrees with previous work performed by this group in which a crystalline chromium phosphate with six hydration waters was produced at room temperature, but green, x-ray amorphous solids were produced that were apparently anhydrous at temperatures of 50 and 80 degress (10). Crystalline violet chromium phosphate behaves as a simple electrovalent salt, ionizing to yield the hexa aquo chromium cation and phosphate (39). The temperature dependence of the form of precipitate is not surprising then, considering the kinetic behavior of the chromium (+3) ion with respect to ligand exchange. At low temperature the hexa aquo ion behaves as a simple trivalent cation with an effective radius (radius of Cr(+3) + 2 times radius H_2O) (40). The precipitated chromium salt retains the color of the solvated hexa aquo ion. At higher temperatures ligand replacement rates increase significantly, reducing the hydration of the chromium ion as well as changing its absorption spectrum. The rate determining step of the nucleation process is quite likely related to the ligand replacement of primary hydration water molecules by some particular phosphate specie.

A convenient set of experimental conditions for studying chromium phosphate precipitation in acidic solutions with a view toward gaining some insight into the rate controlling steps leading to the depletion of chromium from solution is obtained by conducting the precipitation in a medium of excess phosphate buffered at a pH slightly above pK1 (2.23). In this system the pH will remain fairly constant during the precipitation, and complication of side reactions involving chromium hydroxide precipitation are avoided. Further, excess phosphate allows the effect of increasing chromium to be tested. A temperature of 65°C was selected as one which would provide rates convenient for taking data. The raw data for a series of experiments in which varying concentrations of hexa aqua chromium ion were added to buffered 1M solutions are shown in Figures 6.38 and 6.39. Prior to the depletion of chromium from solution, an induction period is observed in which nucleation and the initial stages of agglomeration occur (41). The initial decrease in chromium concentration can be approximated by linear regression to estimate the length of the induction period for each test. These values appear in Table 6.17 along with T, the estimated length of the induction period. For the lower chromium concentrations the length of the induction period is approximately inversely proportional to the initial chromium concentration. For the highest chromium concentration studied thus far (0.165 M) the induction period is over twice as long as may be expected. The chromium concentration curves are somewhat complex, some of which is due to precision. Note the slopes for the two lowest concentrations, essentially experimental replicates would have a relative standard deviation of 12%.

The solids obtained in all experiments thus far were green in color, amorphous, and filter well. They are somewhat different than the solids obtained by Arthur (10) who reported them difficult to filter. The solids remain to be characterized with respect to their hydration and elemental composition.

6.1.1.7.3. Conclusions

The purpose of the kinetic experiments are two fold:

- to explain the behavior of the leach solution during Fe-Cr separation, and

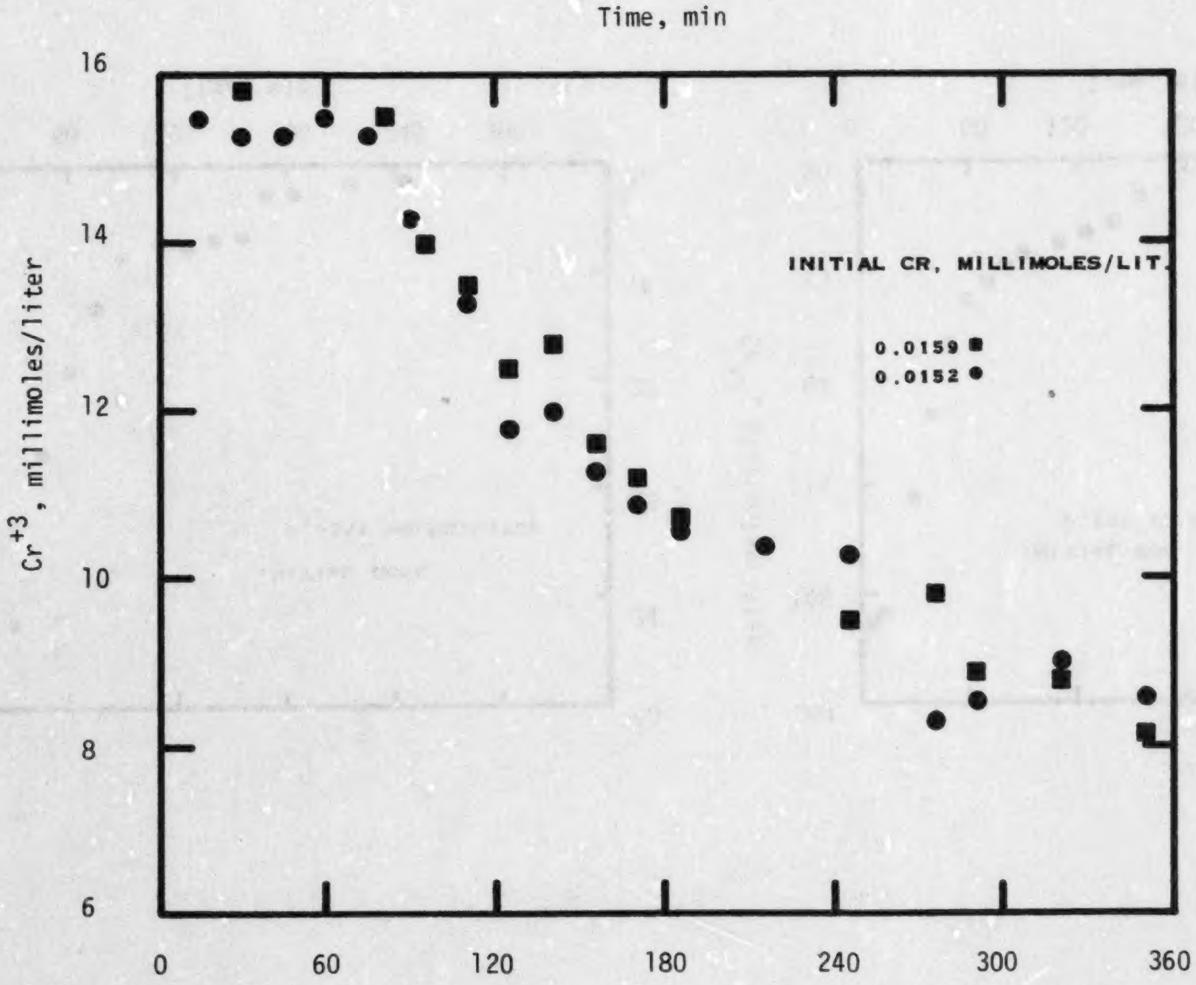

FIGURE 6.38. SOLUTION CHROMIUM CONCENTRATION AS A FUNCTION OF TIME FOR REPLICATE EXPERIMENTS IN 1M PHOSPHATE

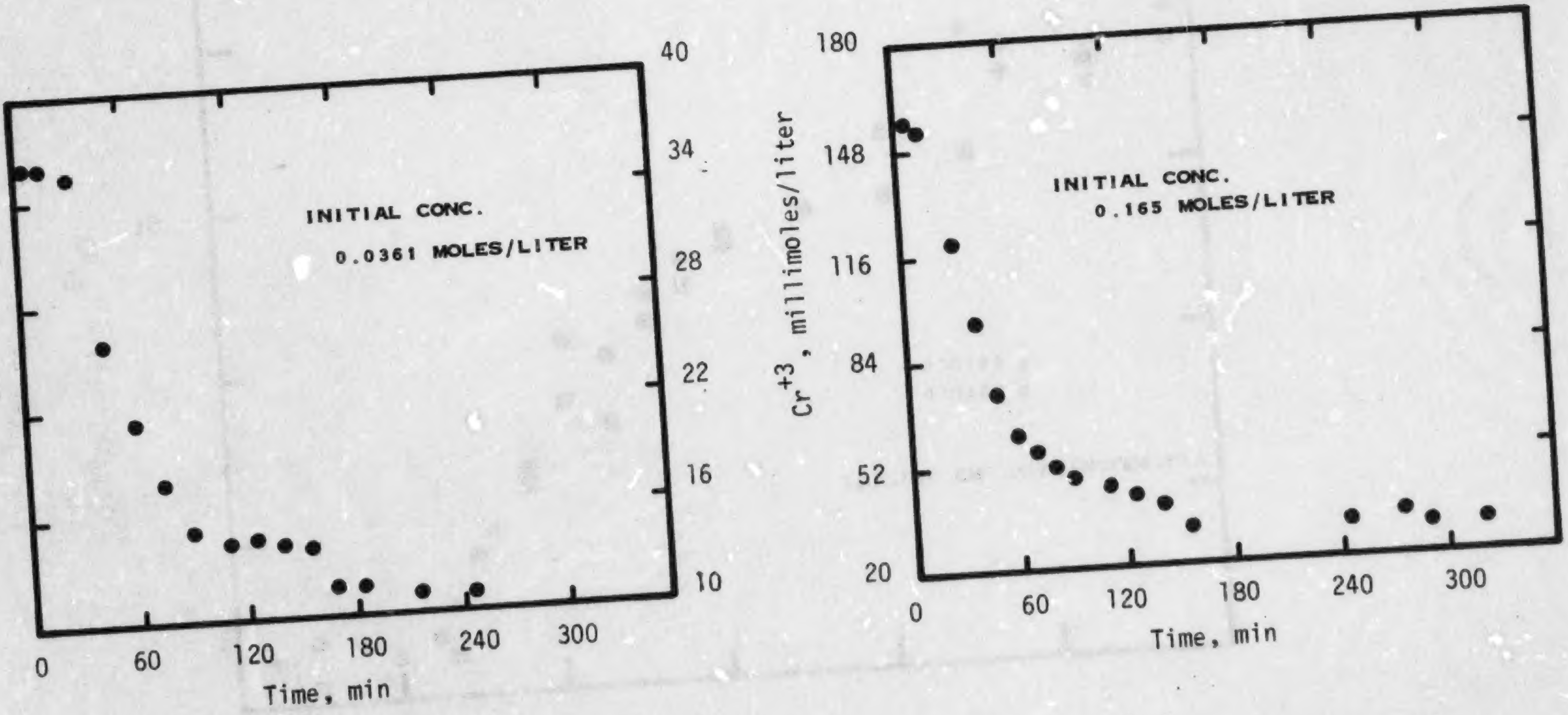

FIGURE 6.39. SOLUTION CHROMIUM CONCENTRATION VERSUS TIME

TABLE 6.17. CHROMIUM PHOSPHATE PRECIPITATION 65°C

Initial Concentration, moles/liter		Cr/ t[a]	I[b]	$[Cr]_s$[c]	pH	
[Cr]	$[PO_4]$				Init.	Final
0.165	1.055	2.30 E-3 (-0.988)	10	-	2.75	1.87
0.0361	0.973	4.66 E-4 (-0.989)	28	6.99 E-3	2.84	2.66
0.0159	0.954	5.19 E-5 (-0.975)	59	6.56 E-3	2.83	2.67
0.0152	0.958	4.35 E-5 (-0.988)	67	6.72 E-3	2.89	2.75

[a] least squares estimate (r value in parentheses), moles/min.

[b] induction time, mins.

[c] estimate of equilibrium chromium concentration; see text.

- provide a set of kinetic parameters that will be useful in the process separation.

The kinetic behavior of a precipitating system is a function of its supersaturation (41). This necessitates a knowledge of the equilibrium relations of the chromium phosphate-water system. Using recent data for chromium hydrolysis products as well as the available data for chromium phosphate solids and complexes, the stability diagram in Figure 6.40 was calculated. Due to the uncertain nature of the solids produced in the reaction, it is still somewhat unclear what the free energies of formation of the precipitated solids actually are.

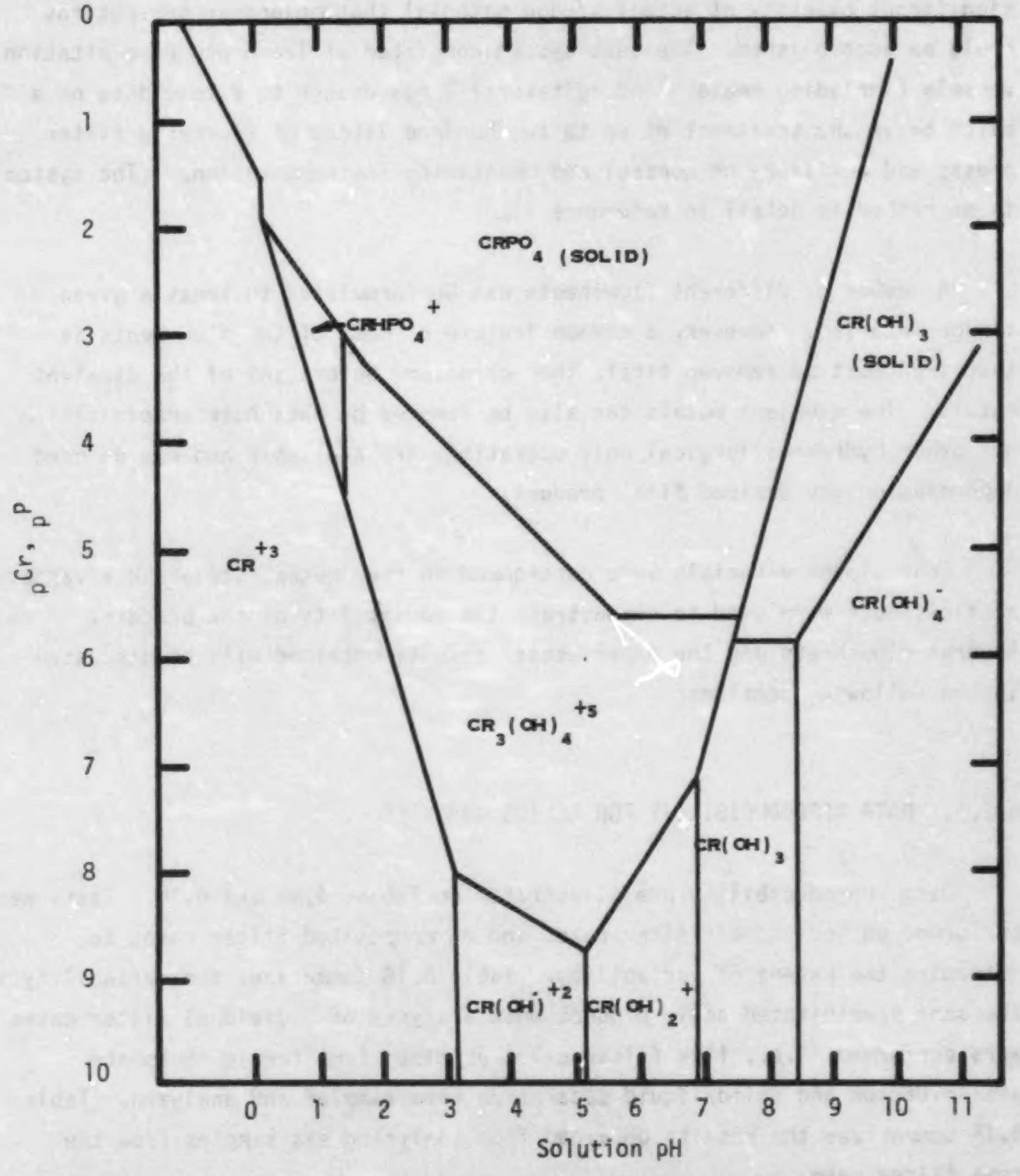

FIGURE 6.40. STABILITY DIAGRAM FOR THE CHROMIUM-PHOSPHATE-WATER SYSTEM USING MOST RECENT DATA FOR CR OLIGOMERS

6.2. LARGE SCALE TEST PROGRAM

The objective of the large scale test work was to demonstrate on a significant quantity of actual sludge material that selective separations could be accomplished. The test system consisted of leach and precipitation vessels (including heaters and agitators) large enough to accommodate on a batch basis the treatment of up to two hundred liters of slurry; a filter press; and auxiliary pH control and monitoring instrumentation. (The system is described in detail in reference 1).

A number of different flowsheets can be formulated to treat a given sludge material. However, a common feature of most of the flowsheets is that iron must be removed first, then chromium, before any of the divalent metals. The divalent metals can also be removed by phosphate precipitation but other hydrometallurgical unit operations are available and may be used depending on the desired final product.

Four sludge materials were considered in the present study and a variety of flowsheets were used to demonstrate the versatility of the process. Several flowsheets and the experimental results obtained will be discussed in the following sections:

6.2.1. DATA REPRODUCIBILITY FOR SOLIDS ANALYSES

Data reproducibility are illustrated in Tables 6.18 and 6.19. Tests were performed on individual filter cakes and on composited filter cakes to determine the extent of variability. Table 6.18 summarizes the variability in the same precipitated solid product when analyses of individual filter cakes were performed, i.e., five filter cakes obtained from ferric phosphate precipitation and solid/liquid separation were sampled and analyzed. Table 6.19 summarizes the results obtained from analyzing six samples from the same filter cake.

TABLE 6.18. ANALYSES OF INDIVIDUAL FILTER CAKES (Lehr Sludge)

Sample No.	Condition	Concentration, Wt.%									
		Fe	Cu	Zn	Cr	Ni	Al	Co	Ti	P	Nb
10170	First Cake	16.13	0.04	0.01	0.22	2.44	0.18	0.12	0.34	9.56	0.08
10172	Second Cake	19.79	0.04	0.02	0.26	2.07	0.18	0.09	0.33	11.44	0.06
10173	Third Cake	16.99	0.03	0.03	0.31	1.87	0.19	0.08	0.26	10.09	0.04
10174	Fourth Cake	15.87	0.04	0.02	0.30	1.87	0.20	0.08	0.24	9.40	0.06
10175	Fifth Cake	23.37	0.03	0.03	0.25	1.79	0.19	0.08	0.19	11.88	0.05
	Average	18.43	0.04	0.02	0.27	2.01	0.19	0.09	0.27	10.47	0.06
		±2.56	±0.01	±.01	±.05	±0.22	±0.01	±0.08	±0.08	±1.07	±0.02

Notes: Test performed on Lehr sludge iron phosphate product.
Solid dissolved using perchlorate digestion procedure.

TABLE 6.19. REPEATED ANALYSES OF COMPOSITED FILTER CAKE (N.I. Sludge)

Sample No.	Concentration, %					
	Fe	Cr	Zn	Al	Ca	P
10321	0.73	13.54	2.30	1.57	0.23	13.56
10322	0.70	12.00	2.20	1.53	0.31	12.60
10323	0.70	12.40	2.36	1.49	0.22	12.35
10324	0.70	12.86	2.31	1.49	0.20	12.88
10325	0.84	13.65	2.44	1.70	0.28	13.62
10326	0.73	12.92	2.17	1.55	0.21	12.89
Average	0.73 ± 0.11	12.90 ± 0.75	2.30 ± 0.10	1.56 ± 0.14	0.24 ± 0.04	12.98 ± 0.64

Notes:
- . Test performed on N.I. sludge chromium phosphate product.
- . See section 6.2.2 for reason zinc content is so high.
- . Solids dissolved using perchlorate digestion procedure.

The accepted procedure for the analyses of solids generated by the large scale test work was to composite the filter cakes, split into a representative sample, dissolve the sample by use of a perchlorate digestion procedure, and analyze the resulting solution by ICP spectrophotometry.

6.2.2. IRON-CHROMIUM-ZINC (N.I. Sludge)

The flowsheet used to treat an iron-chromium-zinc sludge material is presented in Figure 6.41. This material was obtained from an operation engaged in zinc phosphatizing of steel parts and chromium plating final products. Therefore, the sludge was composed primarily of iron-chromium-zinc phosphate. The sludge was high in zinc and chromium with appreciable iron and calcium. Mass flows are included on the flowsheet.

The treatment sequence consisted of acid leaching sufficient sludge to produce 200 liters of starting mixed metal solution containing approximately forty grams per liter dissolved metals; solid/liquid separating the leach residue; oxidizing the ferrous fraction to ferric by air and precipitating ferric phosphate; solid/liquid separating the ferric phosphate; precipitating chromium phosphate at an elevated temperature; solid/liquid separating the chromium phosphate; precipitating zinc phosphate; solid/liquid separating the zinc phosphate.

The starting sludge and product compositions are presented in Table 6.20. The unit operations and experimental conditions are depicted in Figure 6.41. EP toxicity test results on the leach residue are presented in Table 6.21. Elemental distribution among the various products are presented in Table 22. The following general conclusions are noted for this test work:

- Sulfuric acid leaching was very effective in redissolving the metal values; e.g., extraction efficiencies are presented in Table 6.23. The leach unit operation produced 200 liters of a solution containing 3.1 gpl Fe, 2.7 gpl Cr, 3.2 gpl Zn.

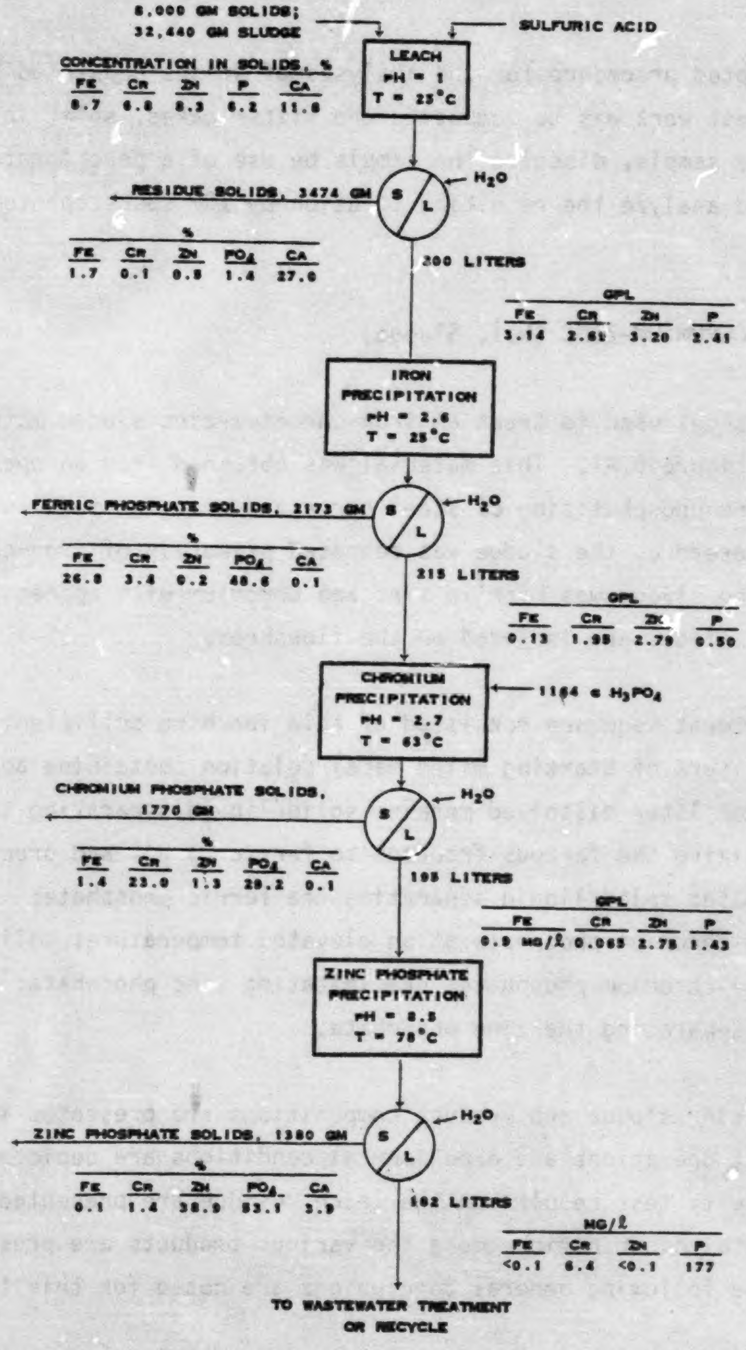
8,000 GM SOLIDS;
32,440 GM SLUDGE
SULFURIC ACID
LEACH
pH = 1
T = 25°C
CONCENTRATION IN SOLIDS, %
FE CR ZN P CA
8.7 6.8 8.3 6.2 11.8
S
L
H2O
RESIDUE SOLIDS, 3474 GM
%
FE CR ZN PO4 CA
1.7 0.1 0.8 1.4 27.0
200 LITERS
GPL
FE CR ZN P
3.14 2.61 3.20 2.41
IRON
PRECIPITATION
pH = 2.6
T = 25°C
S
L
H2O
FERRIC PHOSPHATE SOLIDS, 2173 GM
%
FE CR ZN PO4 CA
26.8 3.4 0.2 48.6 0.1
215 LITERS
GPL
FE CR ZN P
0.13 1.95 2.79 0.50
CHROMIUM
PRECIPITATION
pH = 2.7
T = 63°C
1164 g H3PO4
S
L
H2O
CHROMIUM PHOSPHATE SOLIDS,
1770 GM
%
FE CR ZN PO4 CA
1.4 23.0 1.3 29.2 0.1
195 LITERS
GPL
FE CR ZN P
0.9 MG/ℓ 0.065 2.75 1.43
ZINC PHOSPHATE
PRECIPITATION
pH = 8.5
T = 78°C
S
L
H2O
ZINC PHOSPHATE SOLIDS, 1380 GM
%
FE CR ZN PO4 CA
0.1 1.4 38.9 53.1 3.9
182 LITERS
MG/ℓ
FE CR ZN P
<0.1 6.4 <0.1 177
TO WASTEWATER TREATMENT
OR RECYCLE

FIGURE 6.41. FLOWSHEET FOR THE SEPARATION OF FE-CR-ZN BY PHOSPHATE PRECIPITATION.

TABLE 6.20. PRODUCTS FROM Fe-Cr-Zn LARGE SCALE TEST

Products	Solids, gm	Element Composition, %				
		Fe	Cr	Zn	Ca	PO_4
Fe-Cr-Zn (Starting Solids)	8000	8.67	6.85	8.29	11.83	19.49
Leach Residue	3474	1.69	0.13	0.48	26.97	1.36
Ferric Phosphate	2173	26.75	3.39	0.15	0.05	48.63
Chromium Phosphate	1771	1.38	21.41	1.28	0.14	29.21
Zinc Phosphate	1230	0.09	1.40	33.88	3.93	53.05

TABLE 6.21. EP TOXICITY TEST

System	Fe	Cr	Zn	Ni	Ca	Al	Nb
	Analyses of Leach Solution from Extraction, mg/liter						
Fe-Cr-Zn							
Leach Residue	1.64	1.66	3.44	----	----	----	----
Ferric Phosphate	0.86	0.14	0.37	----	1.91	0.28	----
Fe-Cr-Ni							
Leach Residue and Ferric Phosphate	0.19	<0.00	0.32	5.51	1.40	<0.00	<0.00

Note: EPA designated concentration of chromium for characteristic toxicity is 5.0 mg/liter. Other metals are not listed (23).

TABLE 6.22. ELEMENT DISTRIBUTION RESULTING FROM TREATMENT OF Fe-Cr-Zn SLUDGE

Product	Element Distribution, %			
	Fe	Cr	Zn	Ca
Leach Residue	8.5	0.8	2.6	99.0
Ferric Phosphate	83.8	13.4	0.5	0.1
Chromium Phosphate	3.5	74.3	3.5	0.2
Zinc Phosphate	0.2	3.1	80.9	5.1
Final Solution	<0.0	0.2	<0.0	-

TABLE 6.23. METAL VALUE RECOVERY BY SULFURIC ACID DISSOLUTION

	Element Extracted, %				
	Fe	Cr	Zn	Ca	P
Fe-Cr-Zn	90.0	98.9	96.4	0.6	97.2
	Fe	Cr	Ni	Nb	Ti
Fe-Cr-Ni	93.5	95.9	95.0	0.0	74.6

- The weight of residue resulting from the leach unit operation was about forty percent of the weight of the starting solid. This particular sludge producer uses lime as the neutralizing agent rather than caustic. Therefore, the leach residue was predominantly calcium sulfate (the leach residue weight resulting from most sludge leach solutions neutralized with caustic is about fifteen percent of the starting sludge).

- The residue passed the EP toxicity test (23) and can, therefore, be disposed of in a non-hazardous waste site.

- Ferric phosphate was effectively removed from solution, only 133 mg/liter remained after precipitation. The chromium content of the ferric phosphate solid was only 3.4%.

- The ferric phosphate passed the EP toxicity test. Therefore, if a market does not exist it can be converted to hydroxide (with the regeneration of phosphate reagent) and can be disposed of in a non-hazardous waste site.

- Chromium phosphate was effectively removed from solution, only 90 mg/liter remained after precipitation. The iron content of the product was only 1.4%; the zinc content only 1.3%.

- Zinc phosphate was effectively removed from solution, e.g., <1 mg/liter remained after precipitation. The zinc phosphate contained only 0.11% iron and 1.4% chromium. This material should be marketable as a phosphatizing material.

- The final solution contained only 6.4 mg/liter Cr, <0.1 mg/liter Fe, <0.1 mg/liter Zn. A part of this volume can be recycled as make-up water for the leach operation, i.e., about twenty percent can be recycled. The remainder can be treated by evaporation to produce a sodium sulfate crystalline product.

The filterability of the precipitated phosphates was very good (as was seen earlier in the bench scale test work). An extensive filterability study was conducted on the leach residue, chromium phosphate solids and zinc phosphate solids. The results are presented in Table 6.24.

A second large-scale test (actually performed prior to the above described test) was performed on N.I. sludge using a similar flowsheet but somewhat different unit operation separation conditions. The unit operation conditions were modified as a result of this test in order to achieve the much better results reported above. The product analyses are reported in Table 6.25; the element distribution in Table 6.26.

An alternate flowsheet was also investigated, i.e., leach, solid/liquid separation, coprecipitation of chromium and iron, solid/liquid separation, zinc precipitation. The intent of investigating this flowsheet was that a clean zinc solution or a zinc phosphate solid product could be produced acceptable for internal plant recycle. Also, the precipitated iron and chromium solid could be treated by soda ash fusion to recover chromium while rejecting iron. The composition of the composited filter cake solids are presented in Table 6.27. The element distribution is presented in Table 6.28.

This technique does appear to offer a promising approach for treatment of in-plant sludge that contains iron-chromium-aluminum and zinc.

A short separate bench scale study was conducted on a segregated sludge material, i.e., an iron-zinc sludge. The application of the phosphate process is particularly suited for treating segregated sludges that contain a trivalent cation and a divalent cation such as this phosphatizing sludge, i.e., ferric iron (Fe+3) and zinc (Zn+2).

The iron-zinc sludge is made up of precipitated (in the phosphatizing cell) iron and zinc phosphates (not hydroxides as are the electroplating sludges normally considered in this study). The flowsheet for the treatment of this material is based on choosing a pH at which zinc phosphate will redissolve but iron will not dissolve. The conditions can be effectively predicted from stability diagrams and from experimental data collected in other parts of this study. Therefore, the flowsheet for the treatment of

TABLE 6.24. FILTERABILITY OF SOLID PRODUCTS PRODUCED FROM THE LARGE SCALE Fe-Cr-Zn TEST WORK

Product	Equation	Plant Scale-Up	
		Area, ft.^{2}	Cycle Time Min.
Leach Residue ($CaSO_4 \cdot 2H_2O$)	$\alpha = 9.1 \times 10^8 (\Delta P)^{0.85}$	2230	33.3
Chromium Phosphate	$\alpha = 1.5 \times 10^9 (\Delta P)^{0.70}$	2953	25.0
Zinc Phosphate	$\alpha = 2.6 \times 10^8 (\Delta P)^{0.93}$	----	----
Iron-Chromium-	$\alpha = 2.0 \times 10^9 (\Delta P)^{0.74}$	----	----

Notes: • α = cake resistance.
ΔP = pressure drop across cake.
•Filter press used was an Ingersol-Rand 360.
•Area based on treatment of 50 tons of solids per eight-hour day at a P of 80 psi.
•Cycle time includes: cake formation time, air dry time, wash time, air dry time, dump time.

TABLE 6.25. PRODUCTS FROM Fe-Cr-Zn PRELIMINARY LARGE SCALE TEST

Product	Conditions	Solid gms.	Element Composition, %					
			Fe	Cr	Zn	Ca	Al	P
Fe-Cr-Zn (starting solids)		8000	2.92	8.70	10.85	7.08	1.08	3.42
Leach Residue	48-65°C, 1 hr.	3880	1.03	0.26	0.73	24.4	0.74	0.41
Ferric Phosphate	Dichromate Oxidation 25°C, 1 hr., pH=2.2	713	23.18	3.9	0.22	0.37	1.06	13.50
Chromium Phosphate	70°C, 1 hr., 85°C, 3 hrs., pH=3.0	5360	0.73	12.90	2.30	0.24	1.56	12.98
Zinc Phosphate	20°C, 0.5 hr., pH=5.9	368	0.40	6.7	25.8	0.5	----	11.2
Final Solution	----	----	0.025	0.050	1.92	0.36	0.03	1.56

TABLE 6.26. ELEMENT DISTRIBUTION RESULTING FROM PRELIMINARY TREATMENT OF Fe-Cr-Zn SLUDGE

Product	Element Distribution, %					
	Fe	Cr	Zn	Ca	Al	P
Leach Residue	17.1	1.4	3.3	76.3	19.1	5.8
Ferric Phosphate	70.6	4.0	0.2	0.2	5.0	35.1
Chromium Phosphate	16.7	99.5	14.2	0.9	55.6	55.8
Zinc Phosphate	0.6	3.5	10.9	0.3	——	2.0
Final Solution	1.7	1.1	63.0	10.2	——	20.0
Accountability, %	106.7	109.5	91.6	87.6	——	118.7

Notes: ·Based on ICP analyses of solids.
·Conditions were inappropriate to effectively remove the zinc.

TABLE 6.27. PRODUCTS FROM Fe-Cr COPRECIPITATION LARGE SCALE TESTS

Product	Conditions	Element Composition, %					
		Fe	Cr	Zn	Ca	Al	P
Fe-Cr-Zn (Starting Solids)		2.94	6.00	6.42	5.20	1.23	2.76
Leach Residue	20°C, 0.5 hr.	0.89	0.45	0.77	10.75	0.08	0.49
Ferric-Chromium Phosphate	90°C, 1 hr. pH=3	4.36	5.90	3.78	0.3	2.02	13.56
Zinc Phosphate	90°C, pH=5.9	0.16	0.39	30.01	11.3	0.12	14.34
Final Solution, gpl		<0.001	<0.001	----	<0.001	<0.001	0.71

TABLE 6.28. ELEMENT DISTRIBUTION RESULTING FROM COPRECIPITATION OF IRON AND CHROMIUM FROM LARGE SCALE TEST

Product	Solids, gms	Element Distribution, %					
		Fe	Cr	Zn	Ca	Al	P
Starting Solids	8135	----	----	----	----	----	----
Leach Residue	3615	13.5	3.3	5.3	91.9	2.8	7.9
Ferric-Chromium Phosphate	4810	87.8	94.5	34.8	3.4	94.8	55.0
Zinc Phosphate	1500	0.6	0.7	51.7	24.0	1.1	10.9
Solution	——	0.0	0.0	0.0	0.0	0.0	10.8
Accountability, %		101.9	98.5	91.8	119.3	98.9	84.6

this material consists of: redissolution of the zinc phosphate in acid (can be sulfuric, phosphoric, or nitric); and separation of ferric phosphate by filtration (and disposed of by adding to the plant sludge circuit). This leaves a high zinc-phosphate bearing solution for recycle to the phosphatizing plant circuit. The equipment requirements are simple, e.g., simple stirred reactors and filter devices.

The results of several acid leach tests performed on the iron-zinc sludge at a nominal pH of two are presented in Table 6.29. The goal was to reject iron while producing a solution that contained approximately fifteen grams per liter zinc. This objective was achieved for all the tests performed, i.e., iron was not leached but zinc was effectively redissolved.

6.2.3. IRON-CHROMIUM-NICKEL (Lehr Sludge)

The flowsheet used to treat an iron-chromium(+6)-nickel sludge is presented in Figure 6.42. This material was a sludge produced by an electrochemical machining facility. It contained the chromium in a mixed valence state.

The starting sludge and solids composition are presented in Table 6.30. EP toxicity test results for ferric phosphate were presented in Table 6.21 earlier. Elemental distribution among the various products are presented in Table 6.31. The following general conclusions are noted for this test work:

- Sulfuric acid leaching was very effective in redissolving the metal hydroxides of iron, chromium, and nickel. Some of the nickel present in the starting sludge was present as metallic particles (along with niobium) that do not readily redissolve. If the leach residue could be separated, it would be a high value product because of its nickel and niobium content, e.g., the residue (which makes up about 9% of the starting solids) contains 19.3% Ni, 43.1% Nb, and 7.2% Ti.

The high nickel-niobium fraction was not separated in the present test

TABLE 6.29. IRON-ZINC SLUDGE TREATMENT FOR ZINC DISSOLUTION

Condition	Concentration, gpl		
	Zn	Fe	P
Starting Sludge, % (66% solids)	10.9	16.0	-
Phosphoric Acid Leach pH = 2.0	15.68	0.37	29.69
Phosphoric Acid Leach pH = 2.5	13.23	0.02	13.36
Phosphoric Nitric Leach pH = 2.5	13.50	0.02	9.12
Nitric Acid Leach pH = 2.0	15.82	0.01	5.59
Bonderite Diluted pH = 1.8	15.88	0.02	4.48

Notes:
- 0.616 gm wet sludge added to 2.8 liters of water. Acid added to maintain pH. 20°C.
- Bonderite diluted is simply diluting the zinc phosphate solution presently used by N.I. for zinc make-up.

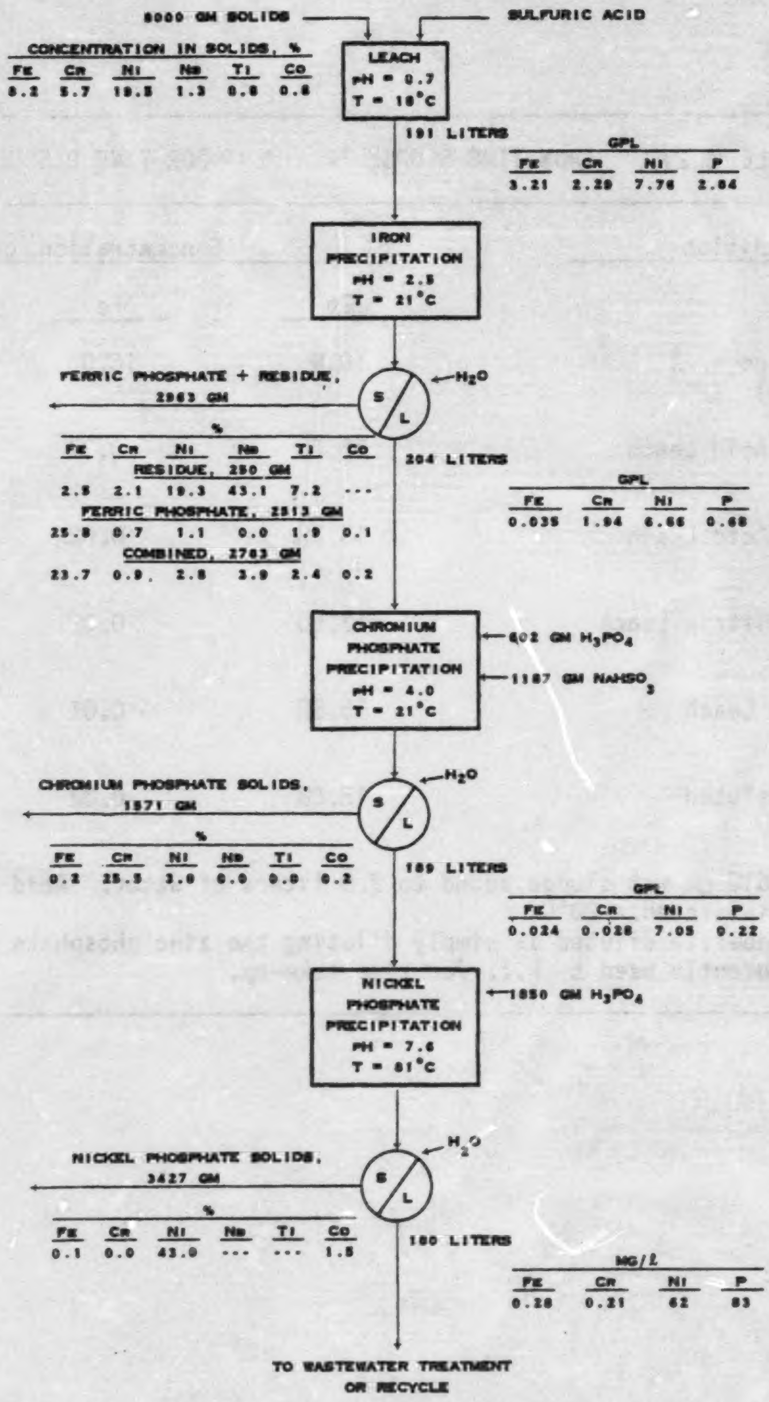
8000 GM SOLIDS
SULFURIC ACID
CONCENTRATION IN SOLIDS, %
FE CR NI NB TI CO
8.2 5.7 19.5 1.3 0.8 0.6
LEACH
pH = 0.7
T = 18°C
191 LITERS
GPL
FE CR NI P
3.21 2.29 7.76 2.84
IRON PRECIPITATION
pH = 2.5
T = 21°C
FERRIC PHOSPHATE + RESIDUE, 2963 GM
H_2O
S
L
%
FE CR NI NB TI CO
RESIDUE, 250 GM
2.5 2.1 19.3 43.1 7.2 ---
FERRIC PHOSPHATE, 2513 GM
25.8 0.7 1.1 0.0 1.9 0.1
COMBINED, 2763 GM
23.7 0.9 2.8 3.9 2.4 0.2
204 LITERS
GPL
FE CR NI P
0.035 1.94 6.66 0.68
CHROMIUM PHOSPHATE PRECIPITATION
pH = 4.0
T = 21°C
602 GM H_3PO_4
1187 GM $NaHSO_3$
CHROMIUM PHOSPHATE SOLIDS, 1571 GM
H_2O
S
L
%
FE CR NI NB TI CO
0.2 25.5 3.0 0.0 0.0 0.2
189 LITERS
GPL
FE CR NI P
0.024 0.028 7.05 0.22
NICKEL PHOSPHATE PRECIPITATION
pH = 7.6
T = 81°C
1850 GM H_3PO_4
NICKEL PHOSPHATE SOLIDS, 3427 GM
H_2O
S
L
%
FE CR NI NB TI CO
0.1 0.0 43.0 --- --- 1.5
180 LITERS
MG/ℓ
FE CR NI P
0.28 0.21 62 83
TO WASTEWATER TREATMENT OR RECYCLE

FIGURE 6.42. FLOWSHEET FOR THE SEPARATION OF FE-CR-NI BY PHOSPHATE PRECIPITATION

TABLE 6.30. PRODUCTS FROM Fe-Cr-Ni LARGE SCALE TEST

Products	Solids, gms	Element Composition, %							
		Fe	Cr	Ni	Ca	PO_4	Nb	Ti	Co
Starting Solids	8000	8.20	5.73	19.49	-	-	1.33	0.83	0.80
Leach Residue Plus Ferric Phosphate	2763	23.67	0.87	2.79	0.76	46.61	3.86	2.39	0.24
Chromium Phosphate	1571	0.19	25.53	2.99	0.92	48.82	0.01	0.02	0.18
Nickel Phosphate	3427	0.06	0.02	43.04	1.46	43.37	-	-	1.54

TABLE 6.31. ELEMENT DISTRIBUTION RESULTING FROM TREATMENT OF Fe-Cr-Ni SLUDGE

Product	Element Distribution, %					
	Fe	Cr	Ni	Nb	Ti	Co
First Solids						
Metallic Residue	1.0	1.2	3.1	101.3	28.1	0.0
Ferric Phosphate	99.0	4.1	1.8	0.0	74.6	7.9
Chromium Phosphate	0.4	87.6	3.0	-	-	4.9
Nickel Phosphate	0.5	0.2	94.6	-	-	80.3
Final Solution	<0.0	<0.0	0.7	-	-	-

work because the available filter press cloths were not appropriate to make the separation.

- The leach unit operation produced 191 liters of solution containing 3.21 gpl Fe, 2.29 gpl Cr, and 7.76 gpl Ni.

- Ferric phosphate was precipitated from the solution containing the metallic particle residue. The iron content remaining in solution was only 35 mg/liter. The ferric phosphate solid contained only 0.87% Cr but was, of course, high in nickel, niobium, and titanium, because of the presence of the unfiltered metallic fraction, e.g., 2.79% Ni, 3.86% Nb, and 2.39% Ti.

  The EP test results (Table 6.21) showed only nickel above one hundred times the drinking water standard. However, if the metallic fraction had been separated the ferric phosphate solid would have passed the EP test.

- Chromium phosphate was effectively removed from solution, only 28 mg/liter of chromium remained after precipitation. The iron content of the product was only 0.18%, the nickel content was 2.99%. Chromium phosphate would have to be converted to a more marketable product such as chromic oxide by a simple pyrometallurgical fusion process. The nickel would be separated from the chromium during the fusion conversion process.

- Nickel phosphate was removed to a level of 62 mg/liter nickel. Further lowering can be achieved by precipitating at a higher pH.

  The solid nickel phosphate product contained only 0.06% Fe but contained 1.54% Co.

- The final solution contained 0.28 mg/liter Fe, 0.21 mg/liter Cr, and 62 mg/liter Ni. A part of this volume can be recycled as make-up water for the leach operation. The remainder can be treated by evaporation to produce a sodium sulfate crystalline product and a solution more concentrated in nickel and chromium for recycle to the leach unit operation.

A second large-scale test was performed on the Lehr sludge (actually performed prior to the above described text). It allowed for the successful conditions described in the previous flowsheet to be set. The results showed good separability and product purity, Table 6.32, similar to the previously described test.

6.3. ALTERNATE FLOWSHEETS

A large number of flowsheets can be developed to treat mixed metal sludges. The general philosophy followed in the phosphate study was that it was necessary to first remove trivalent metal cations before attempting to separate the divalent cations. This approach was followed in all cases except where copper was present. Also the philosophy was followed that conversion of the valence state of chromium by oxidation was to be avoided and that simple precipitation separations were preferred (where applicable) over other separation techniques.

A number of variations on the recovery sequence were investigated in this study. A few examples will be presented to illustrate the flexability available to the user of the proposed technology. The illustration will be limited to separation of the trivalent metal cations iron and chromium:

- Ferric cations can be selectively precipitated by phosphate at room temperature from chromium (+3) cations, and solid/liquid separated. The chromium will then precipitate as a phosphate at 60 to 80 degrees. This approach produces a clean ferric phosphate that can be converted to ferric hydroxide with regeneration of the phosphate reagent. The chromium phosphate is also produced as a clean solid that can be converted to other more marketable products.

TABLE 6.32. PRODUCTS FOR THE Fe-Cr-Ni PRELIMINARY LARGE SCALE TEST

Product	Conditions	Element Composition, %						
		Fe	Cr	Ni	P	Nb	Ti	Co
Starting Solids	----	8.17	5.73	19.49	----	1.33	0.83	0.80
Ferric Phosphate and Leach Residue	25°C, 0.5 hr.,	18.43	0.27	2.01	10.47	0.06	0.27	0.09
Chromium Phosphate	70-75°C, 0.5 hr., pH=3.3	1.13	22.43	0.30	12.39	0.06	0.03	0.02
Nickel Phosphate	50-60°C, 1 hr., pH=6.0	0.48	1.00	21.86	9.44	----	0.03	1.29
Final Leach, gpl	----	0.01	0.003	2.09	0.66	0.003	<0.001	0.0017

Note: *Nickel is high in ferric phosphate - leach residue solid because the undissolved metallic fraction is present.

- Ferric cations can be reduced to the ferrous state by addition of powdered iron, and chromium can be precipitated at an elevated temperature (ferrous cations will not precipitate at low pH values) as a phosphate, and solid/liquid separated. Then ferrous cations can be rather easily oxidized by air to the ferric state and precipitated as a phosphate. This flowsheet has an advantage if copper is present in the solution because copper will cement (precipitate) onto the powdered iron and can thereby be separated from solution.

- Ferric and chromium (+3) cation can be coprecipitated together to separate them both from the aqueous divalent ions, the precipitated mixture can be converted to chromic acid with the rejection of iron as an oxide by soda ash fusion.

The choice of the final flowsheet to be used will, of course, depend on the markets for the products and the economic consequences of choosing a particular set of individual unit operations.

6.4. ECONOMIC ANALYSIS

6.4.1. FLOWSHEET

The flowsheet results presented in Section 6.2 illustrate that metal values can be recovered from electroplating and electromachining sludge waste materials. The major advantages of using phosphate precipitation over other possible separation unit operations are the simplicity of the precipitation and ease of solid/liquid separation. Both of these occurrences mean that the process, capital, and operating costs are decreased when compared to other hydrometallurgical operations such as solvent extraction and high temperature precipitation.

A large number of alternative flowsheets are possible. The selection of the most appropriate treatment sequence for a mixed metal sludge material will depend on the products desired and product marketability. The emphasis of this study has been directed toward the separation of iron and chromium from mixed metal leach solutions. While little effort has been expended in this phase of the study to develop a flowsheet to treat the divalent cations, past research at Montana Tech has emphasized divalent cation recovery (1,2). Therefore, a flowsheet to treat a multielement solution can be presented.

A flowsheet capable of effectively treating a multielement solution is presented. It is certainly not the only flowsheet that could be used in an industrial plant but it is a one that would be appropriate and it supplies a basis for performing an economic analysis and sensitivity of cost to plant size analysis. The flowsheet subjected to cost evaluation includes the following unit operations:

- copper solvent extraction-electrowinning.
- iron removal by phosphate precipitation with conversion of the phosphate to ferric hydroxide for landfill disposal and phosphate reagent regeneration for recycle.
- chromium removal by phosphate precipitation with conversion of the chromium phosphate to chromic oxide by sodium carbonate fusion.
- zinc solvent extraction to produce crystalline zinc sulfate.
- nickel solvent extraction-electrowinning.
- recycle of a portion of the final solution as make-up water and treatment of the remainder of the solution by evaporation and recycle to the leach operation.qf

6.4.2. COST ESTIMATE

The following cost summary is presented as a first order estimate for the flowsheet presented in Figure 6.43. Itemized equipment lists were used where possible and literature quoted cost figures were used when available. Costs were estimated using the data of Mular (15) and Word (16). All costs have been updated to first quarter 1987 using the Marshall and Stevens (M&S) Index. The current M&S Index value is 832.7. Major cost items have been included. The factored capital cost totals take care of minor equipment, instrumentation, process piping, auxiliary engineering costs, and plant size factor. Detailed cost sheets, both for capital and operating costs, are presented in Appendix Section 8.2.

This is not a detailed engineering cost analysis. It is only what Mular and Wood claim for the calculational technique, i.e., a first order estimate. Mular suggests that the cost totals will be within ±30 percent. If cost were not available for the present unit operations but data existed for a similar commercial unit operation the sixth tenths rule was used, i.e.,

$$\text{cost} = \text{cost}_{\text{known}} [\text{capacity}_{\text{present}}/\text{capacity}_{\text{known}}]^{0.6} (\text{M\&S}_{\text{now}}/\text{M\&S}_{\text{then}})$$

The potential value of products and reagent costs were obtained from current literature quotations and are reported in Tables 6.33 and 6.34.

The return on investment (ROI) was calculated by the equation:

$$\text{ROI} = \frac{(\text{Value of Products-Annualized Cost})(\text{tax rate})(100)}{\text{Capital Cost}}$$

The cost estimate is based on the flowsheet presented in Figure 6.43. Capital cost and operating cost were estimated. These estimates are presented

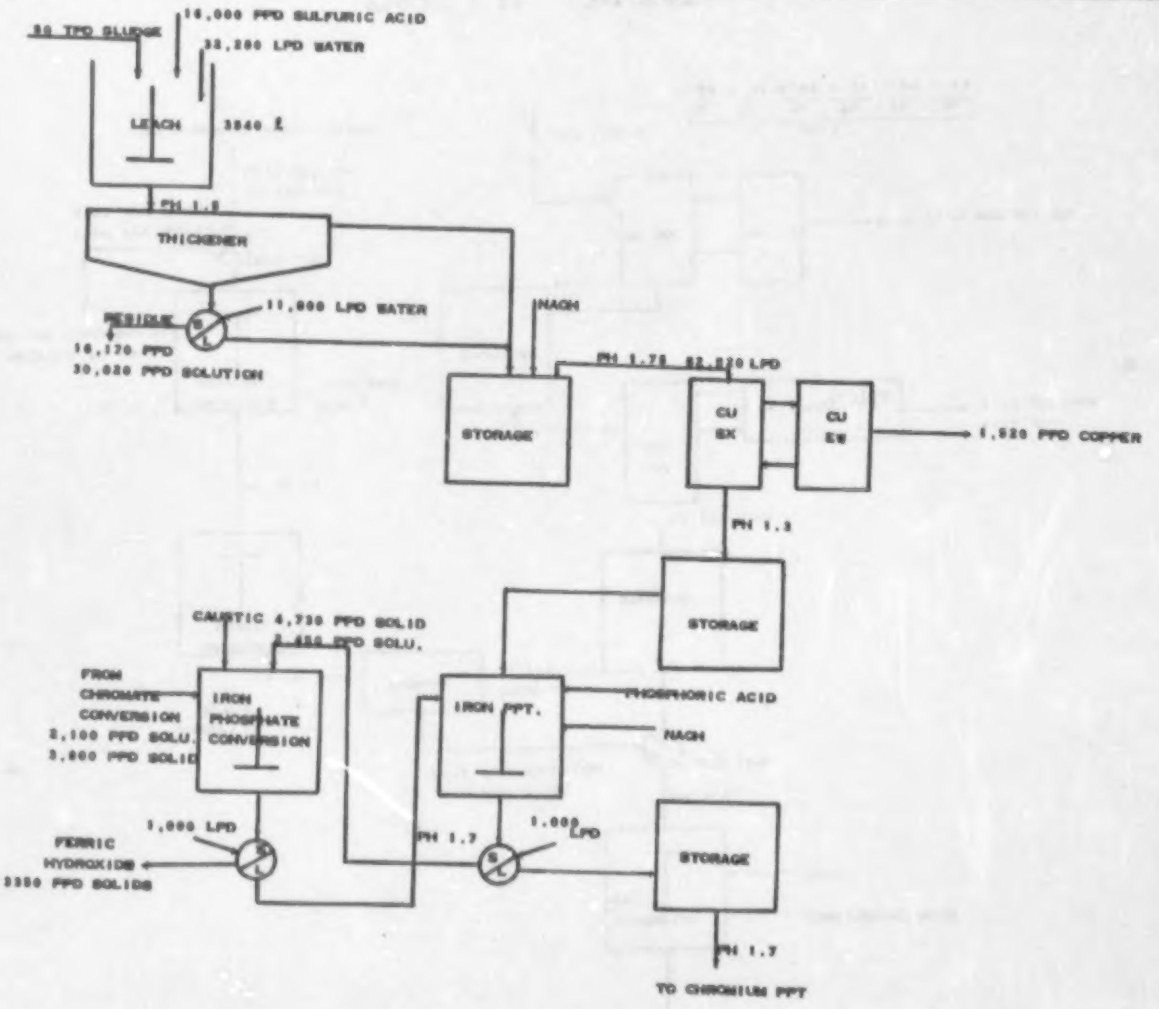
50 TPD SLUDGE
16,000 PPD SULFURIC ACID
32,200 LPD WATER
LEACH
3840 ℓ
PH 1.8
THICKENER
11,000 LPD WATER
RESIDUE
S
L
16,170 PPD
30,020 PPD SOLUTION
NACH
STORAGE
PH 1.75
82,820 LPD
CU
SX
CU
EW
1,520 PPD COPPER
PH 1.3
STORAGE
CAUSTIC 4,730 PPD SOLID
2,450 PPD SOLU.
FROM
CHROMATE
CONVERSION
2,100 PPD SOLU.
3,800 PPD SOLID
IRON
PHOSPHATE
CONVERSION
IRON PPT.
PHOSPHORIC ACID
NACH
1,000 LPD
FERRIC
HYDROXIDE
3350 PPD SOLIDS
S
L
PH 1.7
1,000 LPD
S
L
STORAGE
PH 1.7
TO CHROMIUM PPT

FIGURE 6.43. FLOWSHEET FOR THE TREATMENT OF 50 TPD OF MIXED METAL SLUDGE

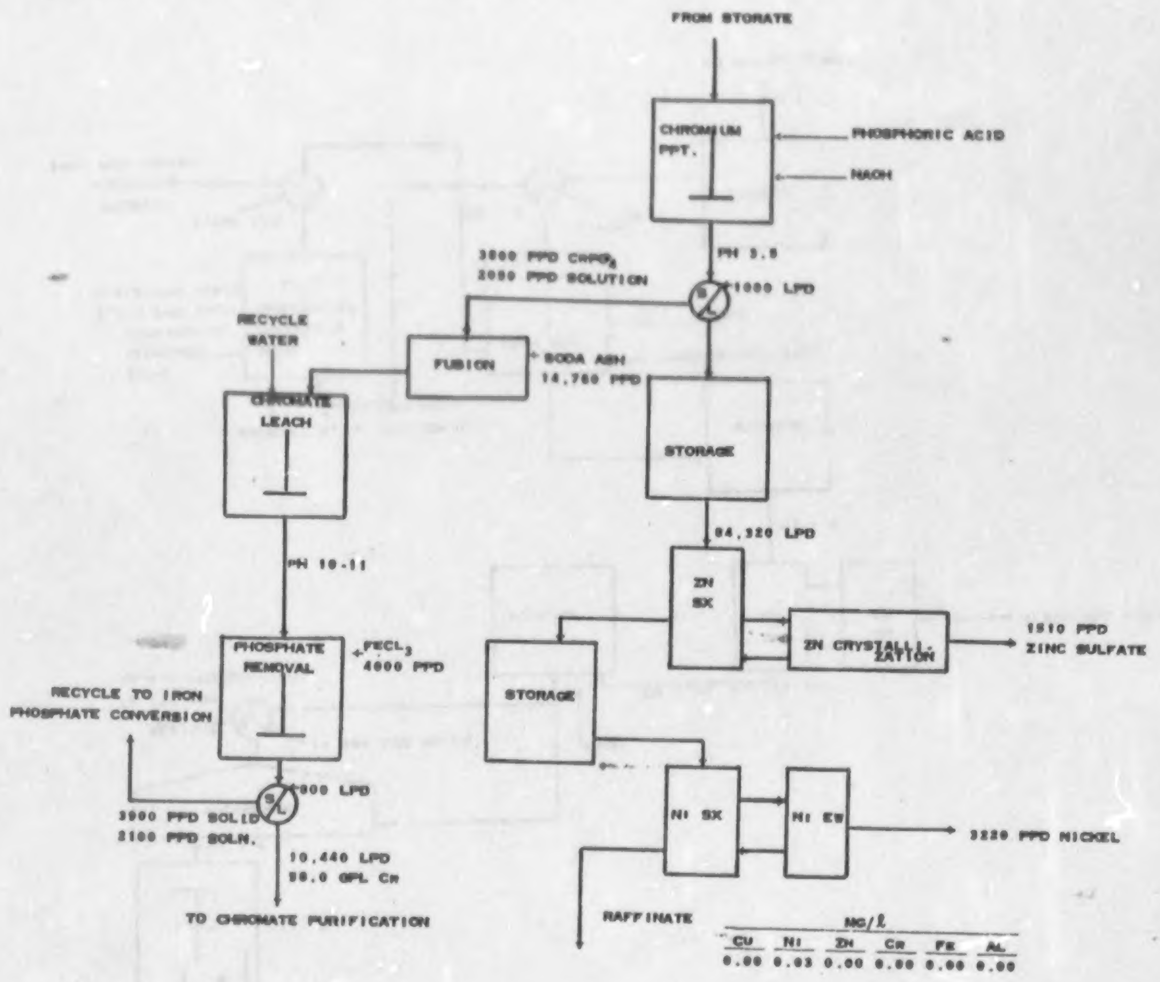
FROM STORATE
CHROMIUM PPT.
PHOSPHORIC ACID
NAOH
PH 3.8
S L
1000 LPD
3800 PPD CRPO$_4$
2050 PPD SOLUTION
FUSION
SODA ASH 14,760 PPD
RECYCLE WATER
CHROMATE LEACH
STORAGE
84,320 LPD
ZN SX
ZN CRYSTALLIZATION
1510 PPD ZINC SULFATE
PH 10-11
PHOSPHATE REMOVAL
FECL$_3$ 4000 PPD
STORAGE
RECYCLE TO IRON PHOSPHATE CONVERSION
S L
800 LPD
3900 PPD SOLID
2100 PPD SOLN.
10,440 LPD
50.0 GPL CR
TO CHROMATE PURIFICATION
NI SX
NI EW
3220 PPD NICKEL
RAFFINATE
MG/ℓ
CU 0.00
NI 0.03
ZN 0.00
CR 0.00
FE 0.00
AL 0.00

FIGURE 6.43. CONTINUED

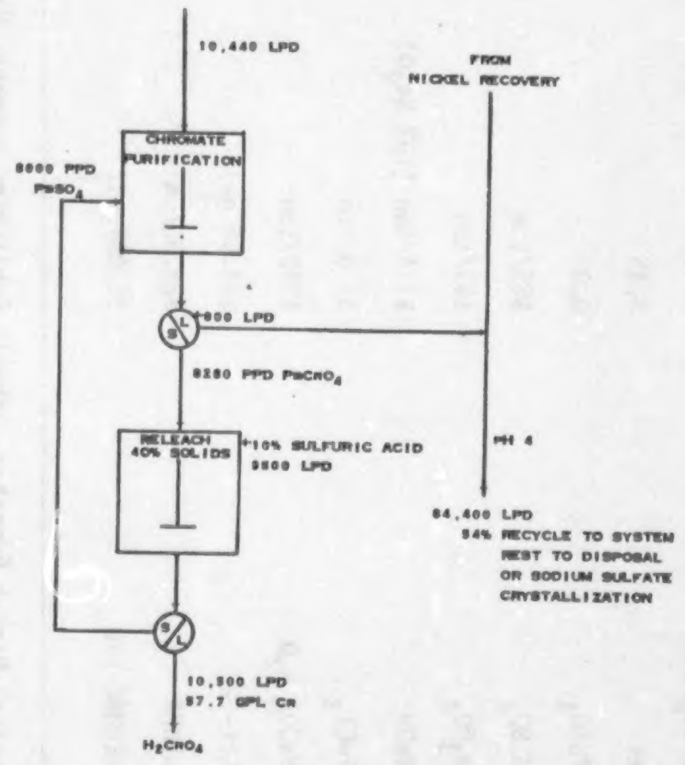
10,440 LPD
FROM
NICKEL RECOVERY
CHROMATE
PURIFICATION
8000 PPD
$PbSO_4$
800 LPD
8280 PPD $PbCrO_4$
RELEACH
40% SOLIDS
10% SULFURIC ACID
9500 LPD
PH 4
84,400 LPD
54% RECYCLE TO SYSTEM
REST TO DISPOSAL
OR SODIUM SULFATE
CRYSTALLIZATION
S
L
10,500 LPD
87.7 GPL Cr
H_2CrO_4

FIGURE 6.43. CONTINUED

TABLE 6.33. VALUE OF PRODUCTS AND REAGENTS LIST

Product or Reagent	Cost ($/pound)
Cu	0.62
H_2CrO_4	1.18
$ZnSO_4 \cdot H_2O$	0.30
Ni	3.45
$PbSO_4$	0.87
H_2SO_4	$85/ton
H_3PO_4	$61/ton
NaOH	$175/ton (76% Na_2O)
$FeCl_3$	$176/ton
$NaCO_3 \cdot H_2O$	$392/ton
LIX-622	$45.60/gal.
DEHPA	$21.30/gal.
KERMAC 510	$1.09/gal.

Inorganics: Chemical Market Reporter, Schnell Publishing Company, May 25, 1987, pp. 32-40.

Organics : Henkel current price list.

TABLE 6.34. TOTAL PRODUCT VALUE FOR 50 TPD COST ESTIMATE

Product	Quantity (pounds/yr.)	Potential Value ($/yr.)
1. Cu	501,600	311,000
2. H_2CrO_4	999,800	1,179,800
3. $ZnSO_4 \cdot H_2O$	499,000	149,700
4. Ni	1,062,600	3,666,000
5. Credit for Disposal ($125/ton)	50 TPD	2,062,500
	Total (1, 2, 3, 4)	5,306,500
	Total (1, 2, 3, 4, 5)	7,369,000

in Appendix Section 8.2. Equipment costs were based on cost equations of the form:

$$\text{Cost}_{\text{now}} = a(\text{capacity})^{b}(\text{M\&S}_{\text{now}}/\text{M\&S}_{\text{then}})$$

where a and b are constants for a particular piece of equipment. The constants a and b are provided for a variety of types of equipment by Mular and Woods.

An equipment list was prepared for each series of unit operations and the cost estimated as described above. The Factored Capital Cost was determined by using the factors as presented in Table 6.35. An annualized cost was then determined based on a five year period at a 12 percent interest rate. An operational cost for the series of unit operations was established based on reagent consumption, manpower requirements, maintenance and power consumption.

The results of the calculations are presented in Tables 8.5 - 8.12.

Operating cost estimates are presented in Table 8.5. The operating cost estimates do not include personnel other than operational personnel. The estimates include: unit operations cost; manpower requirements; maintenance costs; and energy cost.

The ROI calculations were based on the following assumptions: buildings and land are available; the tax rate is 50 percent; interest rate is 12 percent; the pay-off period is five years; and the plant operates for 330 days per year. The quantity of material to be treated is based on 50 tpd of sludge containing 32.69 weight percent solids. The sludge composition is presented in Table 6.36.

Mass balances were based on actual experimental data generated during this study. The mass balance results were used to size the necessary equipment and are reported in Section 8.2.

TABLE 6.35. FACTORED CAPITAL COST ESTIMATE

	Cost (M&S = 832.7)
1. Purchased Equipment Costs	
2. Installed Equipment Costs (1.4 x Item 1)	
3. Process Piping (30% of 2)	
4. Instrumentation (10% of 2)	
5. Auxiliaries (5% of 2)	
6. Outside Lines (5% of 2)	
7. Total Physical Plant Costs (Sum of 2 through 6)	
8. Engineering and Construction (20% of 7)	
9. Contingencies (15% of 7)	
10. Size Factor (Small Commercial, 10% of 7)	
11. TOTAL PLANT FIXED CAPITAL COST (Sum of 7 through 10)	
YEARLY COST, Based on 60 month pay-off period, 12% interest	

TABLE 6.36. COMPOSITED SLUDGE COMPOSITION

Element	Concentration, %
Cu	5.0
Fe	5.1
Cr	4.3
Zn	1.8
Ni	10.4
Al	0.4
Ca	0.9
Si	15.0
P	3.0

Notes:
- Sludge contains 32.69% solids. Analysis above refers to percent in solids.
- Composition is based on equal mix of seven sludges studied.

The first order estimate return on investment based on the flowsheet presented in Figure 6.43 and Table 6.37 is:

$$\mathrm{ROI} = \frac{(5{,}306{,}500-2{,}634{,}100)(2.5)(100)}{2{,}235{,}600}$$

$$= 60 \pm 18\%$$

If a credit is included for the cost of disposal, the return on investment is:

$$\mathrm{ROI} = \frac{(7{,}369{,}000-2{,}634{,}100)(0.5)(100)}{2{,}235{,}600}$$

$$= 106 \pm 32\%$$

The sensitivity of the return on investment to plant size is presented in Tables 6.38 and 6.39 and Figure 6.43. Note that a reasonable return on investment requires a plant capacity of greater than thirty tons per day.

TABLE 6.37. PROCESS COST: FIRST ORDER ESTIMATE

Unit Operation	Cost,$			
	F.C.C.	F.C.A.C.	Yearly Operating	Total Yearly Cost
1. Leach, S/L Separation	335,500	118,300	272,900	391,200
2. Residue Ponding	64,900	22,900	-	22,900
3. Copper SX-EW	354,000	124,800	51,200	176,000
4. Iron Precipitation, Conversion, S/L Separation	221,700	78,100	85,000	163,100
5. Chromium Precipitation, S/L Separation	102,300	36,100	199,800	235,900
6. Chromium Phosphate Fusion, Chromate Leach, Phosphate Removal, S/L Separation	253,900	89,500	1,107,700	1,197,200
7. Chromate Purification, S/L Separation, Releach, S/L Separation	201,300	71,000	29,200	100,200
8. Zinc SX, Zinc Sulfate Crystalization	436,600	153,900	61,900	215,800
9. Nickel SX-EW	265,400	93,500	38,300	131,800
	2,235,600	788,100	1,846,000	2,634,100

TABLE 6.38. PROCESS COST AS A FUNCTION OF PLANT CAPACITY

Unit Operation	Total Yearly Cost, $			Factored Capital Cost, $		
	50 TPD	30 TPD	10 TPD	50 TPD	30 TPD	10 TPD
1. Leach, S/L	391,200	287,900	148,900	335,500	246,900	127,700
2. Residue Ponding	22,900	16,900	8,700	64,900	47,800	24,700
3. Copper SX-EW	176,000	129,500	67,000	354,000	260,600	134,800
4. Iron Precipitation, Conversion, S/L	163,100	120,000	62,100	221,700	163,200	84,400
5. Chromium Precipitation, S/L	235,900	173,600	89,800	102,300	75,300	38,900
6. Chromium Phosphate Fusion, Chromate Leach, Phosphate Removal, S/L	1,197,200	881,200	455,800	253,900	186,900	96,700
7. Chromate Purification,S/L, Releach, S/L	100,200	73,700	38,100	201,300	148,200	76,600
8. Zinc SX, Zinc Sulfate Crystalization	215,800	158,800	82,200	436,600	321,300	166,200
9. Nickel SX-EW	131,800	97,000	50,200	265,400	195,300	101,000
	2,634,100	1,938,600	1,002,800	2,235,600	1,645,500	851,000

TABLE 6.39. PROCESS COST AND RETURN ON INVESTMENT AS A FUNCTION OF PLANT CAPACITY

Plant Size	F.C.C., $	Total, $/yr	R.O.I., %	
50 TPD	2,235,600	2,634,100	60 ± 18	106 ± 32*
30 TPD	1,645,500	1,938,600	38 ± 11	75 ± 23*
10 TPD	851,000	1,002,800	3 ± 1	27 ± 8*

NOTE: *Credit taken for disposal.

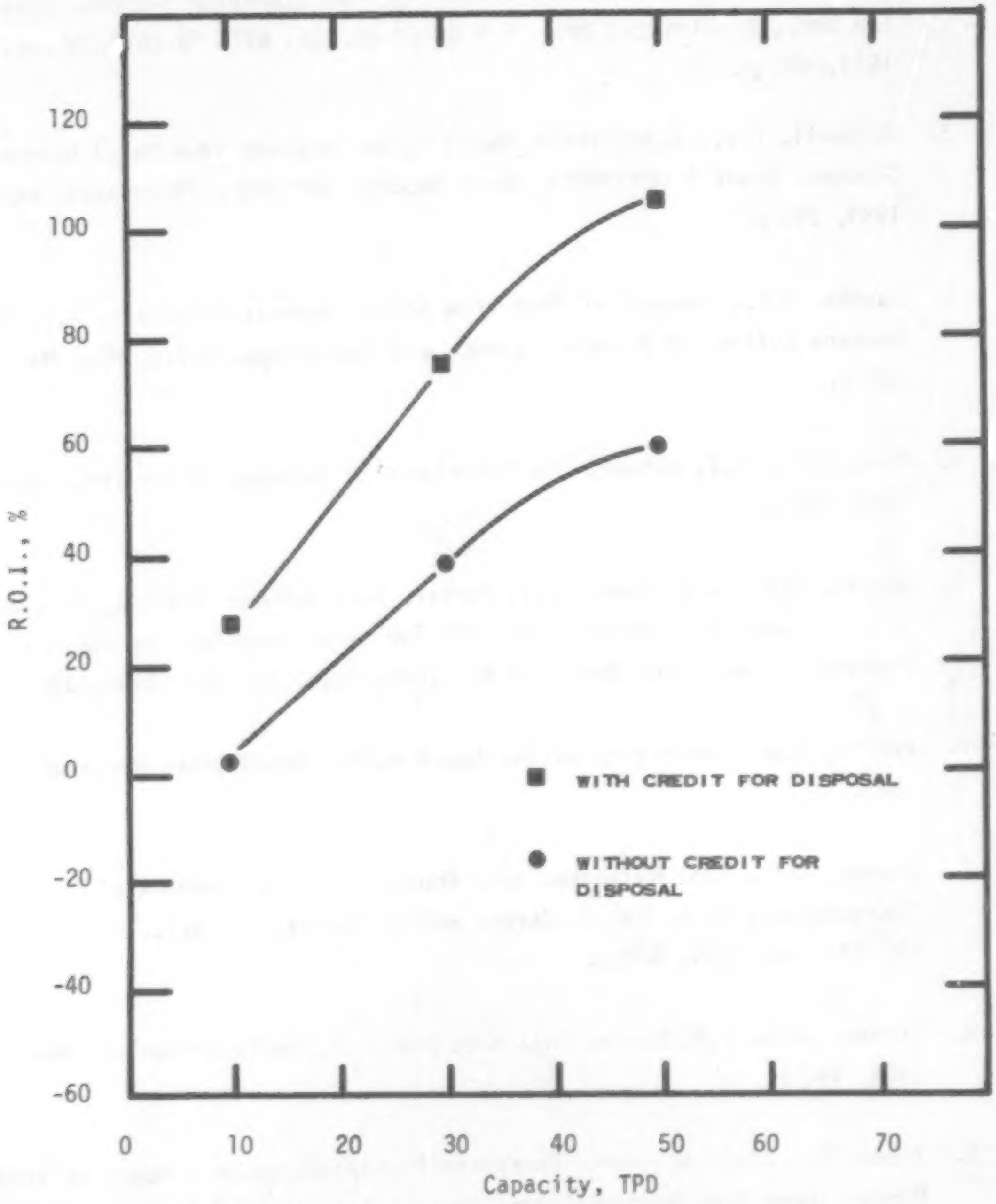

FIGURE 6.44. RETURN ON INVESTMENT AS A FUNCTION OF PLANT CAPACITY

SECTION 7

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APPENDICES

SECTION 8

APPENDICES

8.1. ANALYTICAL PROCEDURES

8.1.1. ANALYTICAL INSTRUMENTATION AND TECHNIQUES

A description of the analytical instrumentation used in this study is presented in Table 8.1.

8.1.1.1. ICP

Multielement and single element standards were obtained from SPEX, Inc., and contained all the elements of interest in the present study. Precision of the PE ICP was taken as the coefficient of variation of three readings normally performed for calibration and usually was 1% or less for 100 mgpl standards. Aqueous samples were collected and stored in 25 ml polyethylene vials. Appropriate dilutions were performed in class A volumetric glassware with sample dispensing performed with an Oxford micropipettor. Literature supplied by the manufacturer of this pipettor device suggests an accuracy of 1% and precision of 1% at the 1.0 ml capacity. Aliquots were produced by introduction of a sample in a 1% HCl solution. The HCl diluent was used to stabilize iron in solution. Blanks of the 1% reagent grade HCl solution were occasionally analyzed for elemental concentrations and always produced negligible results.

8.1.1.2. XRD

X-ray diffraction analysis was performed with a Norelco system which incorporates a 2.5 KW X-ray generator and vertical goniometer. The generator was operated at 35 KV accelerating voltage with a tube current of 15 mA. A copper target tube with a nickel K filter attached was

TABLE 8.1. ANALYTICAL INSTRUMENTATION.

Application	Designation	Model
Aqueous Solution Analyses	Inductively Coupled Plasma	Perkin-Elmer ICP - 5500
Aqueous Solution Acidity (pH)	pH Measurement	Orion 601 Ionalyzer
. Probes	Combination Electrode with Silver/ Silver Chloride Reference, High Temperature Capabilities.	Broadley-James Corporation LC 209301-3-Sc LC 31332-3-Sc
	Combination Redox	Orion 96-78-00
Digested Solid Samples	Induction Coupled Plasma	Perkin-Elmer ICP - 5500
Solid Analyses		
. Phase Identification	X-ray Diffraction	Norelco 2.5 KW Generator
. Elemental Make-up and Concentration	Scanning Electron Microscopy With Energy Dispersive x-ray Analyzer	International Scientific Instruments ISI - 40 With Princeton Gamma Tech System 4.
. Particle Size and Shape	Optical Microscope Scanning Electron Microscope	Olympus BH International Scientific Instruments.

installed in the instrument for these analyses. Samples were prepared by grinding a portion of the blended sample to 100% minus 325 mesh. The powder then was placed in an aluminum sample holder with a sample depth of approximately 3/16", which was sufficient depth to ensure diffraction analysis of the sample and not the sample holder. Relative peak intensities and d-spacings were indexed and calculated by hand from the resulting X-ray diffraction trace and sample identification was accomplished through correllation of the experimental trace with X-ray diffraction data cards published by the "Joint Committee on Chemical Analysis by X-Ray Diffraction Methods".

8.1.1.3. SEM-EDX

Electron microscopy analysis was performed with an International Scientific Instruments, ISI-40 microscope which has a Princeton Gamma Tech System 4 energy dispersive X-ray analyzer attached. Semi-quantitative analysis calculations were performed with the bulk sample analysis program available in the PGT System 4. This program calculates the analyses of unknown spectras based on a library of standard spectras stored in the system's memory. Sample preparation for SEM photograph usually entailed mounting the powder on a sample stub with phosphorus-free, graphite paint. After the paint had dried, the sample was either carbon or gold coated to improve its electrical conductivity and then photographed at various magnifications with the ISI-40 instrument.

8.1.2. SLUDGE DISSOLUTION AND ANALYSES FOR LARGE SCALE TESTS

The dissolution of the sludge material was performed by the following procedure:

- A 40-100 pound sample was removed from the barrel of sludge. The sludge was chopped up with a laboratory mixer into pea size particles.

- The sample was blended by repeated mixing.
- One hundred gram samples were split from the blended material and placed in a drying oven at 100°C for 24 hours. Samples were weighed and moisture contents calculated. Samples were run in quadruplicate to verify results.
- The dried material was ground in a mortar and pestle to -100 mesh. A 5.00 gram sample was split from the ground material.
- The dried and sized sample was digested to determine composition.
- A 5.00 gm sample was carefully weighed and placed in a 400 cc beaker. 100cc of aqua regia was added to the beaker plus 25 cc of perchloric acid.
- The slurry was placed on a hot-plate and fumed to a semi-dry state. The sample was cooled and redissolved in 100 cc of 10% HCl solution.
- The solution was transferred to a 500 ml volumetric flask and diluted to volume. A reagent blank was carried along through the entire procedure for matrix correction.
- The digested sample solution was analyzed for element content by ICP spectrophotometry.

8.1.3. AQUEOUS PHASE ANALYSES

Aqueous phase analyses were performed by ICP (Perkin-Elmer 5500) procedures. A solution sample was withdrawn from a test sequence, filtered (if necessary), placed in a 25 cc polyethylene vial and capped. The sample was assigned an analytical number in a master record book. Each sample number was recorded and a brief one line description written beside it. Dilution, if any, of the solution was recorded in the test notebook. The sample was then supplied to the project's chemist. Most samples were analyzed within three days by ICP sectrophotometric analysis. All dilutions performed by the chemist are reported in the analytical computer print-out for each individual sample. All results from the analytical laboratory were reported in mg/liter.

8.1.3.1. Performance Test Results

An EPA performance evaluation set of aqueous samples was supplied to Montana Tech for determination of solution metal contents. The results are presented in Table 8.2.

The results of the performance evaluation showed that all elelments of interest to the present study were rated acceptable (99% confidence interval) except for iron (sample one). The reason the iron sample was not acceptable was because of a calculational reporting error, i.e., the values should have been 0.593 mg/liter which places the analysis within the acceptable range.

8.1.3.2. Technical Systems Audit Results

A Technical Systems Audit was conducted on the present project on March 10, 1987, QA ID Number: R-107B-TS(S). This report and the written response is available from the EPA Project Officer, Mr. John Martin.

The major problem identified by the Technical Systems Audit was that precision data were not collected as was specified in the Quality Assurance Plan for the project. This situation was corrected by performing replicate and spike analyses on ten percent of all samples collected. The results of the performance test work are presented in Table 8.3. The results demonstrated that the original data were valid; that reproducibility and spike recoveries were excellent.

8.1.4. FERRIC/FERROUS

It was desirable to analyze a number of samples for the Fe^{++}/Fe^{+++}

TABLE 8.2. PERFORMANCE EVALUATION REPORT: 11/19/86 WATER POLLUTION STUDY NUMBER WP 017

Parameter	Sample No.	Montana Tech Value, mg/liter	True Value, mg/liter	Acceptable Limits, mg/liter	Warning Limits, mg/liter	Performance Evaluation
Al	1	0.361	0.390	0.303 - 0.517	0.331 - 0.490	Acceptable
	2	0.149	0.156	0.109 - 0.211	0.121 - 0.198	Acceptable
Cd	1	0.0868	0.100	0.0827 -0.115	0.0867 - 0.111	Acceptable
	2	0.0429	0.050	0.0404 -0.0571	0.0425 - 0.0550	Acceptable
Cr	1	0.0724	0.090	0.0695 -0.107	0.0742 - 0.103	Check for Error*
	2	0.0471	0.060	0.0446 -0.00726	0.0481 - 0.0691	Check for Error
Cu	1	0.198	0.224	0.194 - 0.249	0.201 - 0.242	Check for Error
	2	0.0187	0.0224	0.0159 - 0.0288	0.0175 - 0.0272	Acceptable
Fe	1	0.566	0.0672	0.572 - 0.738	0.593 - 0.718	Not Acceptable**
	2	0.0530	0.0672	0.0494 - 0.0825	0.0536 - 0.0784	Check for Error
Ni	1	0.234	0.245	0.205 - 0.284	0.215 - 0.274	Acceptable
	2	0.0424	0.0490	0.0371 - 0.0613	0.0401 - 0.0583	Acceptable
Zn	1	0.273	0.304	0.255 - 0.348	0.267 - 0.337	Acceptable
	2	0.0175	0.0190	0.0134 - 0.0257	0.0149 - 0.0242	Acceptable

Notes: * Check for Error: The reported value was within the acceptance limit, i.e., technically acceptable, but since the value was outside of the warning limits (95% confidence interval) a marginal problem may exist.

** Not Acceptable: The reported value was beyond the acceptance limits. See text for comments.

TABLE 8.3. REPLICATE AND SPIKE ANALYSES

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10023	Original	44.52	----	5.95	57.88
	Duplicate	43.60	----	6.10	58.85
	CV, %	1.48	----	1.77	1.18
	Spike	53.27	10.58	16.31	67.78
	Recovery, %	92.1	105.8	102.8	94.1
10030	Original	1.78	----	----	2.61
	Duplicate	2.00	----	----	2.80
	CV, %	----	----	----	2.48
	Spike	12.62	10.45	10.77	12.91
	Recovery, %	107.3	104.5	107.7	102.0
10045	Original	38.72	----	2.09	48.85
	Duplicate	36.31	----	2.02	47.36
	CV, %	4.54	----	2.41	2.19
	Spike	46.31	10.40	12.08	57.55
	Recovery, %	87.9	104.0	100.2	94.4
10057	Original	2.01	----	----	----
	Duplicate	2.22	----	----	----
	CV, %	7.02	----	----	----
	Spike	12.51	10.40	10.46	10.52
	Recovery, %	103.9	104.0	104.6	105.2
10062	Original	32.41	----	----	3.56
	Duplicate	31.13	----	----	3.48
	CV, %	2.85	----	----	1.61
	Spike	41.43	10.35	9.95	13.20
	Recovery, %	96.6	103.5	99.5	96.8
10078	Original	18.61	----	----	0.454
	Duplicate	18.03	----	----	0.480
	CV, %	2.23	----	----	3.94
	Spike	28.05	10.47	9.92	10.21
	Recovery, %	97.3	104.7	99.2	97.4

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ Zn	Ni	Fe	Cr
10088	Original	5.86	----	1.77	5.71
	Duplicate	5.45	----	1.64	5.25
	CV, %	5.13	----	5.39	5.96
	Spike	16.23	10.63	11.51	15.26
	Recovery, %	105.7	106.3	98.0	97.8
10099	Original	4.54	----	----	----
	Duplicate	4.59	----	----	----
	CV, %	0.77	----	----	----
	Spike	15.03	10.50	9.98	9.71
	Recovery, %	104.6	105.0	99.8	97.1
10108	Original	35.38	----	1.831	0.15
	Duplicate	35.09	----	1.62	0.14
	CV, %	0.58	----	8.61	4.88
	Spike	46.24	11.49	11.50	9.82
	Recovery, %	110.0	114.9	97.7	96.7
10113	Original	----	----	----	----
	Duplicate	----	----	----	----
	CV, %	----	----	----	----
	Spike	10.43	10.58	10.37	9.92
	Recovery, %	104.3	105.8	103.7	99.2
10247	Original	0.19	76.84	----	0.09
	Duplicate	0.17	77.23	----	0.11
	CV, %	7.86	0.36	----	14.14
	Spike	10.67	87.85	10.05	10.25
	Recovery, %	104.9	108.2	100.5	101.5
10251	Original	0.41	72.36	----	----
	Duplicate	0.38	68.78	----	----
	CV, %	5.37	3.59	----	----
	Spike	10.88	[illegible]1.61	10.11	9.91
	Recovery, %	104.8	1[illegible]2.4	101.1	99.1

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10301	Original	----	2.39	1.19	----
	Duplicate	----	2.22	1.23	----
	CV, %	----	5.21	2.34	----
	Spike	10.43	13.26	11.95	10.46
	Recovery, %	104.3	109.5	107.4	104.6
10315	Original	----	2.41	0.90	----
	Duplicate	----	2.20	0.81	----
	CV, %	----	6.44	7.44	----
	Spike	9.78	13.03	11.17	10.20
	Recovery, %	97.8	107.2	103.1	102.0
10328	Original	21.02	1.66	----	----
	Duplicate	22.78	1.71	----	----
	CV, %	5.68	2.10	----	----
	Spike	31.56	12.52	10.96	10.03
	Recovery, %	96.6	108.3	109.6	100.3
10334	Original	144.11	1.53	----	----
	Duplicate	141.63	1.68	----	----
	CV, %	1.23	6.61	----	----
	Spike	153.31	12.49	10.82	9.80
	Recovery, %	104.4	108.8	108.2	98.0
10344	Original	142.68	----	0.858	----
	Duplicate	140.33	----	0.823	----
	CV, %	1.17	----	2.94	----
	Spike	152.51	9.93	10.66	10.36
	Recovery, %	110.0	99.3	98.2	103.6
10354	Original	13.64	----	0.234	----
	Duplicate	12.93	----	0.197	----
	CV, %	3.78	----	12.14	----
	Spike	22.67	10.37	10.21	9.97
	Recovery, %	93.8	103.7	99.9	99.7

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10363	Original	6.74	0.397	----	----
	Duplicate	6.43	0.412	----	----
	CV, %	3.33	2.62	----	----
	Spike	17.01	10.61	10.23	9.66
	Recovery, %	104.2	102.0	102.3	96.6
10375	Original	15.56	----	----	----
	Duplicate	15.93	----	----	----
	CV, %	1.66	----	----	----
	Spike	25.02	10.63	10.51	10.03
	Recovery, %	92.7	106.3	105.1	100.3
10382	Original	----	----	----	----
	Duplicate	----	----	----	----
	CV, %	----	----	----	----
	Spike	10.03	10.52	10.56	9.94
	Recovery, %	100.3	105.2	105.6	99.4
10388	Original	54.57	----	13.91	5.02
	Duplicate	51.91	----	14.69	5.09
	CV, %	3.53	----	3.86	0.98
	Spike	62.64	10.66	24.53	15.41
	Recovery, %	107.3	106.6	98.4	103.2
10397	Original	18.96	----	----	3.40
	Duplicate	18.84	----	----	3.50
	CV, %	0.47	----	----	2.03
	Spike	28.97	10.58	10.29	13.53
	Recovery, %	101.3	105.8	102.9	100.3
10401	Original	----	----	3.78	----
	Duplicate	----	----	3.66	----
	CV, %	----	----	2.21	----
	Spike	9.29	9.75	13.32	9.55
	Recovery, %	92.9	97.5	96.6	95.5

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10420	Original	104.00	----	21.78	9.23
	Duplicate	101.39	----	22.41	8.93
	CV, %	1.80	----	2.02	2.34
	Spike	112.54	10.76	31.13	18.88
	Recovery, %	98.4	107.6	90.3	98.0
10430	Original	113.56	----	0.813	4.39
	Duplicate	112.90	----	0.827	4.26
	CV, %	0.41	----	1.21	2.12
	Spike	123.68	10.54	10.79	14.51
	Recovery, %	104.5	105.4	99.7	101.8
10449	Original	114.52	----	33.00	10.98
	Duplicate	114.73	----	33.96	11.14
	CV, %	0.13	----	2.03	1.02
	Spike	125.70	10.72	44.43	20.86
	Recovery, %	110.7	107.2	109.5	98.0
10451	Original	95.54	----	----	0.845
	Duplicate	96.23	----	----	0.774
	CV, %	0.51	----	----	6.20
	Spike	106.78	10.12	10.28	11.16
	Recovery, %	108.9	101.2	102.8	103.5
10469	Original	112.15	----	----	4.90
	Duplicate	110.31	----	----	4.38
	CV, %	1.17	----	----	7.92
	Spike	121.31	11.12	10.28	14.52
	Recovery, %	100.8	111.2	102.8	98.8
10477	Original	111.17	----	33.51	10.57
	Duplicate	112.01	----	33.56	11.01
	CV, %	0.53	----	0.08	2.88
	Spike	122.58	10.70	43.44	20.87
	Recovery, %	109.9	107.0	99.0	100.8

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10487	Original	0.10	----	----	----
	Duplicate	0.13	----	----	----
	CV, %	18.4	----	----	----
	Spike	10.42	10.68	9.83	10.18
	Recovery, %	103.0	106.8	98.3	101.8
10495	Original	29.67	----	17.24	24.61
	Duplicate	29.34	----	17.23	23.80
	CV, %	0.79	----	0.04	2.37
	Spike	39.73	10.45	27.13	33.54
	Recovery, %	102.2	104.5	98.9	93.3
10505	Original	34.35	----	5.48	23.49
	Duplicate	34.51	----	5.37	22.59
	CV, %	0.33	----	1.43	2.76
	Spike	45.08	10.25	15.21	32.41
	Recovery, %	106.5	102.5	97.8	93.7
10516	Original	----	68.13	9.76	20.66
	Duplicate	----	66.61	8.80	20.24
	CV, %	----	1.59	7.31	1.45
	Spike	10.13	77.39	19.39	30.93
	Recovery, %	101.3	100.2	101.1	104.8
10527	Original	29.76	----	17.20	24.81
	Duplicate	29.40	----	17.81	24.80
	CV, %	0.86	----	2.45	0.04
	Spike	39.31	10.45	27.46	34.87
	Recovery, %	97.3	104.5	96.5	100.6
10538	Original	29.81	----	1.76	21.37
	Duplicate	30.13	----	1.54	20.73
	CV, %	0.75	----	9.43	2.15
	Spike	40.63	10.23	11.51	20.83
	Recovery, %	106.6	102.3	98.6	97.8

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10548	Original	29.40	----	18.66	24.75
	Duplicate	29.54	----	17.67	24.20
	CV, %	0.34	----	3.85	1.59
	Spike	38.98	10.33	27.77	34.11
	Recovery, %	95.1	103.3	96.1	96.4
10551	Original	28.29	----	7.88	24.04
	Duplicate	28.31	----	6.96	23.78
	CV, %	0.05	----	8.77	0.77
	Spike	38.67	10.37	17.41	33.81
	Recovery, %	103.7	103.7	99.9	99.0
10564	Original	23.76	----	0.349	6.53
	Duplicate	25.46	----	0.361	6.56
	CV, %	4.83	----	2.39	0.32
	Spike	35.19	10.63	9.88	17.23
	Recovery, %	105.8	106.3	95.2	106.8
10573	Original	29.92	----	6.48	23.54
	Duplicate	29.41	----	5.45	22.93
	CV, %	1.22	----	12.21	1.86
	Spike	39.52	9.72	15.12	32.54
	Recovery, %	98.5	97.2	91.6	93.1
10581	Original	29.23	----	0.493	18.41
	Duplicate	26.58	----	0.461	17.52
	CV, %	6.71	----	4.74	3.50
	Spike	37.57	9.76	9.47	27.35
	Recovery, %	96.6	97.6	90.0	93.8
10600	Original	0.42	22.86	0.29	18.45
	Duplicate	0.48	71.27	0.23	18.23
	CV, %	9.43	1.56	16.32	0.85
	Spike	10.66	81.83	10.73	28.84
	Recovery, %	102.1	97.6	104.7	105.0

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10605	Original	----	63.60	----	15.60
	Duplicate	----	63.40	----	15.81
	CV, %	----	0.22	----	0.95
	Spike	10.01	73.31	10.41	25.98
	Recovery, %	100.1	98.1	104.1	102.7
10615	Original	0.31	59.44	----	0.102
	Duplicate	0.33	62.25	----	0.098
	CV, %	4.42	3.26	----	2.83
	Spike	11.01	20.54	9.84	10.15
	Recovery, %	106.9	96.9	98.4	100.5
10629	Original	29.70	----	18.29	25.72
	Duplicate	28.93	----	16.90	25.43
	CV, %	1.86	----	5.59	0.80
	Spike	39.81	11.57	27.76	36.68
	Recovery, %	104.9	115.7	101.6	111.0
10636	Original	53.22	----	12.91	5.37
	Duplicate	53.90	----	12.14	5.26
	CV, %	0.90	----	4.35	1.46
	Spike	63.94	10.66	21.97	15.10
	Recovery, %	103.8	106.6	94.4	97.8
10644	Original	0.20	----	----	----
	Duplicate	0.24	----	----	----
	CV, %	12.86	----	----	----
	Spike	9.66	10.04	9.76	9.67
	Recovery, %	94.4	100.4	97.6	96.7
10659	Original	----	----	----	----
	Duplicate	----	----	----	----
	CV, %	----	----	----	----
	Spike	9.34	10.00	9.48	9.91
	Recovery, %	93.4	100.0	94.8	99.1

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10666	Original	32.01	----	31.45	26.90
	Duplicate	32.41	----	29.99	26.84
	CV, %	0.88	----	3.36	0.16
	Spike	42.58	10.31	40.05	36.31
	Recovery, %	103.7	103.1	93.3	94.4
10688	Original	27.91	----	1.33	19.53
	Duplicate	27.05	----	1.24	20.05
	CV, %	2.21	----	4.95	1.86
	Spike	38.11	11.00	12.46	31.29
	Recovery, %	106.3	110.0	111.7	115.0
10693	Original	0.21	----	----	----
	Duplicate	0.19	----	----	----
	CV, %	7.07	----	----	----
	Spike	10.34	10.47	11.08	10.30
	Recovery, %	101.4	104.7	110.8	103.0
10702	Original	27.52	----	----	0.65
	Duplicate	26.56	----	----	0.78
	CV, %	2.51	----	----	12.86
	Spike	36.59	10.78	11.06	11.05
	Recovery, %	95.5	107.8	110.6	103.3
10710	Original	----	7.46	0.29	2.22
	Duplicate	----	7.13	0.21	1.99
	CV, %	----	3.20	22.63	7.73
	Spike	9.99	17.68	10.82	12.32
	Recovery, %	99.9	103.8	105.7	102.1
10726	Original	----	----	----	0.64
	Duplicate	----	----	----	0.58
	CV, %	----	----	----	6.95
	Spike	10.40	10.32	10.73	9.98
	Recovery, %	104.0	103.2	107.3	93.7

TABLE 8.3. REPLICATE AND SPIKE ANALYSES (Continued)

Sample		Concentration, mg/ℓ			
		Zn	Ni	Fe	Cr
10736	Original	----	----	88.13	30.23
	Duplicate	----	----	93.11	30.96
	CV, %	----	----	3.88	1.69
	Spike	10.21	11.77	101.85	41.04
	Recovery, %	102.1	117.7	112.3	104.4
10748	Original	48.62	----	0.51	0.89
	Duplicate	48.12	----	0.58	0.86
	CV, %	0.73	----	9.08	2.42
	Spike	59.17	11.11	11.37	11.22
	Recovery, %	108.0	111.1	108.2	103.4
10756	Original	----	70.80	----	----
	Duplicate	----	68.59	----	----
	CV, %	----	2.24	----	----
	Spike	10.83	79.98	10.99	10.26
	Recovery, %	108.3	102.8	109.9	102.6
10768	Original	52.06	----	----	----
	Duplicate	51.93	----	----	----
	CV, %	0.18	----	----	----
	Spike	62.51	10.88	10.01	10.76
	Recovery, %	105.1	108.8	100.1	107.6

CV = Coefficient Variation

contents. The analytical technique used for Fe^{++} content followed the procedure: The chief interference with the FeII determination is from high Ni concentrations which obscure the endpoint. Thus, a small volume of sample is used and diluted to about 50 ml.

To a 125 ml Erlenmeyer flask add 50 ml H_2O (deionized), 15 ml 20% H_2SO_4, and 2 ml of H_3PO_4. Pipet in 1.0 ml of sample and add 8 drops of sodium diphenylamine sulfonate indicator. Titrate using moderate quantities of dichromate while stirring or swirling. Proceed slowly with small volumes of dichromate near the endpoint. When a violet color persists for one minute, the endpoint has been reahed. It is best to perform triplicate determinations until volumes agree to within ± .02 ml.

Report as gpl using:

$$Fe^{++} \text{ gpl} = \frac{\text{(vol. 0.0001 N dicromate)(55.85)}}{1000}$$

The reagents required for Fe^{++} determination include:

- Potassium dichromate solution (0.2 N) made by drying pure $K_2Cr_2O_7$ @ 120°C and dissolving 4.9040 gm in one liter of deionized H_2O. Dilute to 0.001 N solution.

- H_2SO_4 solution; 20 v/o.

- Sodium diphenylamine sulphonate solution: 0.16 w/o.

- Concentrated H_3PO_4.

The ferric iron content of the aqueous phase was determined by subtracting the Fe^{++} content from the total solution iron content.

Chromate or dichromate anion concentration was determined by the following procedure:

- Determine the total chromium content of the solution by AA or ICP.
- Expose a known volume of solution to an equal volume of IRA 900 (a strongly basic ion exchange resin). This quantitatively removes the $CrO_4^{=}$, $Cr_2O_7^{=}$, or $HCrO_4^{-}$ anions.
- Measure the volume of solution and analyze the recovered solution by AA or ICP.
- Wash the resin with water and collect the wash solution, measure the volume and determine the total chromium content of this sample (Cr+3). Calculate the oxidized chromium in mg.

8.2. DETAILS OF ECONOMIC ANALYSIS

An economic analysis was presented in Section 6.4 for a 50 ton per day facility. The mass flows, equipment lists, factored capital cost data sheets, and operation cost estimates are presented in this section.

8.2.1. LEACH, S/L SEPARATION

The equipment list is presented in Table 8.5 and the factored capital cost (FCC) is presented in Table 8.6. The operating cost summary is presented in Table 8.4.

8.2.2. RESIDUE PONDING

The jarosite ponding cost is estimated from recent cost data on a state of the art mineral processing tailings pond. The result is presented in Table 8.7.

TABLE 8.4. OPERATING COST SUMMARY

	Cost, $/Yr
Leach, S/L Separation	
1. Reagents	
sulfuric acid: 8 tpd	224,400
2. Labor (30%), Maintenance (6%), and Power (5%):	
Total is 41% of Factored Capital Annual Cost	48,500
	272,900
Residue Ponding	
Operating cost included in capital cost estimate	
Cu SX, EW	
1. Reagents recycled: included in capital cost estimate.	
2. As above	51,200
	51,200
Precipitation, Conversion, S/L Separation	
1. Reagents	
phosphoric acid, recycled: included in capital cost estimate.	
caustic: 230 tpy	53,000
2. As above	32,000
	85,000
Chromium Precipitation, S/L Separation	
1. Reagents	
phosphoric acid: 420 tpy	67,600
caustic: 510 tpy	117,400
2. As above	14,800
	199,800

TABLE 8.4. OPERATING COST SUMMARY

		Cost, $/yr
Chromium Phosphate Fusion, Chromate Leach, Phosphate Removal, S/L Separation		
1. Reagents		
sodium carbonate: 2435 tpy		954,800
ferric chloride: 660 tpy		116,200
2. As before		36,700
		1,107,700
Chromate Purification, S/L Separation, Releach, S/L Separation		
1. Reagents		
sulfuric acid: 0.3 tpy		100
lead sulfate: One time cost included in capital cost		
2. As before		29,100
		29,200
Zn SX, Zinc Sulfate Crystallization		
1. Reagents		
DEHPA: 250 gal	5,300	
Kermac 510: 375 gal	400	
HCl: 700 pounds	400	
sulfuric acid: 1 ton	100	
Amberlite LA-2: 320 gal	8,000	
	14,200 One time cost included in capital cost	
Organic loss: 13 mg/liter, 38 gal/yr		900
2. As before		61,000
		61,900

TABLE 8.4. OPERATING COST SUMMARY

			Cost, $/yr
	Ni SX, EW		
1.	Reagents		
	LIX 64: 46 gal	2,100	
	Kermac 510: 260 gal	300	
		2,400 One time cost included in capital cost	
2.	As before		38,300
			38,300

TABLE 8.5. LEACH, SOLID/LIQUID SEPARATION EQUIPMENT LIST

	Cost, $ (M&S=500)
Feed System	
1. Vibratory feeder: $C = 965(20\text{ft}^2)^{0.559}$ 2.5 tph, 1 each	5,200
2. Recycle solution feeder: $C = 156(30\text{gpm})^{0.38}$	600
3. Acid cup feeder: $C\ 1385(1\ \text{cup})^{0.625}$	1,400
Leach System	
4. Leach Tanks: $C = 27.5(440\text{gal})^{0.629}$ s.s. with agitator	2,000
5. Thickener tank: $C = 7.13(7000\text{gal})^{0.791}$ and mechanism: $C = 1110(6.3\text{ft})^{0.965}$, s.s.	14,400
Filtering System	
6. Drum filter: $C = 8235(19\text{ft}^2)^{0.292}$, 2 each.	38,900
7. Repulp tank: $C = 27.5(100\text{gal})^{0.629}$, s.s., 2 each	1,000
8. Storage tank: $C = 0.897(7{,}500\text{gal})^{0.897}$, fiberglass	2,700
TOTAL (M&S = 500)	66,200
TOTAL (M&S = 832.7)	110,200

TABLE 3.6. FACTORED CAPITAL COST FOR LEACH, SOLID/LIQUID SEPARATION SYSTEM

	Cost ($, M@S = 832.7)
1. Purchased Equipment Costs	110,200
2. Installed Equipment Costs (1.4 x Item 1)	154,300
3. Process Piping (30% of 2)	46,300
4. Instrumentation (10% of 2)	15,400
5. Auxiliaries (5% of 2)	7,700
6. Outside Lines (5% of 2)	7,700
7. Total Physical Plant Costs (Sum 2 through 6)	231,400
8. Engineering and Construction (20% of 7)	46,300
9. Contingencies (15% of 7)	34,700
10. Size Factor (Small Commercial, 10% of 7)	23,100
11. TOTAL PLANT FIXED CAPITAL COSTS	335,500
YEARLY COST, Based on 5 year pay-off period, 12% interest.	118,300

TABLE 8.7. RESIDUE PONDING FACTORED COST

The cost for residue ponding storage is estimated by determining the necessary pond capacity. Assumptions include: land is available; pond capacity is great enough for ten year storage; and controllable access is available.

The cost is estimated by ratioing the capacity of a known recent tailing pond as described by Jones (35); i.e., \$6,000,000 (1980 cost) for a capacity of 7.3 million cubic meters; includes pumping, pH control, instrumentation, and monitoring.

The storage capacity needed for the present estimate is 2,360 M^3.

$$\text{Cost} = 6\times10^6(2,360/7.3\times10^6)^{0.6}(832.7/620)$$

$$= 64,900$$

This cost is estimated to be the current factored capital cost. The annualized cost is \$22,900.

TABLE 8.8. COPPER SOLVENT EXTRACTION-ELECTROWINNING EQUIPMENT LIST AND FACTORED CAPITAL COST

The factored capital cost for the solvent extraction system is estimated from fabricated equipment costs for solvent extractors presented by Woods(16):

Data: Mixer-settlers

Size	Size Range	Cost, \$	Exponent	M&S
1.5 lit/s	1.5-10 lit/s	7,000	0.4	600

(Includes: installed mixer-settler, including explosion proof motors, drives, and within module piping, concrete, steel, instruments, electrical, insulation and paint, and necessary labor.)

Factors for Materials

2.00 for 316 s.s., 1.4 for rubber lined, 2.0 for crud removal system.

The capital cost for the present system is:

$$\text{Cost} = 7{,}000(\text{lit/s,present/lit/s,Woods})^{0.4}(\text{M\&S,now/M\&S,then})\text{x}$$

$$(\text{No. of cells})(2.0 \text{ for s.s.})(2.0 \text{ for crud system})$$

$$= 7{,}000(0.96/1.5)^{0.4}(832.7/600)(2)(2)(5) = \$162{,}500$$

The factored capital cost for the electrowinning system is estimated from fabricated equipment costs presented by Woods:

Data:

Size	Size Range	Cost, \$	Exponent	M&S
10^{10} gm/y	2-60x10^{9} gm/y	6x10^{6}	1.0	600

The capital cost for the present system is:

$$\text{Cost} = (6\text{x}10^{6})(2.3\text{x}10^{8}/1\text{x}10^{10})^{1}(832.7/600) = \$191{,}500$$

(Includes: cells, transformers, rectifiers, and electrical distribution)

The capital cost for the present system is:	\$354,000
The FCAC is	124,800
The yearly operation cost is	51,200
The total yearly cost is	176,000

8.2.3. COPPER SOLVENT EXTRACTION-ELECTROWINNING

Copper solvent extraction costs are estimated from data presented by Wood (16). The equipment costs, FCC and FCAC are presented in Table 8.8. The operating cost was presented previously in Table 8.4.

8.2.4. FERRIC PHOSPHATE PRECIPITATION, CONVERSION, S/L SEPARATION

The equipment cost and factored capital cost are presented in Tables 8.9 and 8.10.

8.2.5. CHROMIUM PHOSPHATE PRECIPITATION, S/L SEPARATION

The equipment list is presented in Table 8.11 and the factored capital cost is presented in Table 8.12.

8.2.6. CHROMIUM PHOSPHATE FUSION, CHROMATE LEACH, PHOSPHATE REMOVAL, S/L SEPARATION

The equipment list is presented in Table 8.13 and the factored capital cost is presented in Table 8.14.

8.2.7. CHROMATE PURIFICATION, S/L SEPARATION, RELEACH, S/L SEPARATION

The equipment list is presented in Table 8.15 and the factored capital cost is presented in Table 8.16.

8.2.8. ZINC SOLVENT EXTRACTION, ZINC SULFATE CRYSTALLIZATION

The equipment list and the factored capital cost is presented in Table 8.17.

TABLE 8.9 FERRIC PHOSPHATE PRECIPITATION, CONVERSION, S/L SEPARATION EQUIPMENT LIST

	Cost, \$ (M&S = 500)
Precipitation	
1. Storage Tank: $C = 0.897(7500)^{0.897}$, fiberglass, 2 each.	5,400
2. Precipitation Vessel: $C = 27.5(940\text{gal})^{0.629}$, s.s. with agitator	2,000
3. Solid/Liquid Separation same as item 6 (only one) and 7 in Table .	20,500
Conversion	
4. Reaction tank: $C = 27.5(120\text{gal})^{0.629}$, s.s., with agitator	600
5. Thickener tank: $C = 7.13(500\text{gal})^{0.791}$ and mechanism: $C = 1110(1.25\text{ ft})^{0.965}$, s.s.	2,400
6. Solid/Liquid Separation: $C = 8235(4\text{ft}^2)^{0.292}$	12,400
7. Repulp tank: $C = 27.5(60\text{gal})^{0.629}$, s.s., with agitator	1,100
TOTAL (M&S = 500)	43,700
TOTAL (M&S = 832.7)	72,800

TABLE 8.10. FACTORED CAPITAL COST FOR IRON PRECIPITATION, CONVERSION, SOLID/LIQUID SEPARATION

	Cost ($, M@S = 832.7)
1. Purchased Equipment Costs	72,800
2. Installed Equipment Costs (1.4 x Item 1)	101,900
3. Process Piping (30% of 2)	30,600
4. Instrumentation (10% of 2)	10,200
5. Auxiliaries (5% of 2)	5,100
6. Outside Lines (5% of 2)	5,100
7. Total Physical Plant Costs (Sum 2 through 6)	152,900
8. Engineering and Construction (20% of 7)	30,600
9. Contingencies (15% of 7)	22,900
10. Size Factor (Small Commercial, 10% of 7)	15,300
11. TOTAL PLANT FIXED CAPITAL COSTS	221,700
YEARLY COST, Based on 5 year pay-off period, 12% interest.	78,100

TABLE 8.11. CHROMIUM PHOSPHATE PRECIPITATION, S/L SEPARATION

	Cost, $ (M&S = 500)
1. Precipitation Vessel: $C = 27.5(940)^{0.629}$, s.s. with agitater	2,000
2. Solid/Liquid Separation: $C = 8235(4\text{ft}^2)^{0.292}$	12,400
3. Repulp Tank: $C = 27.5(60\text{gal})^{0.629}$	400
4. Storage Tank: $C = 0.897(7500)^{0.897}$, fiberglass	5,400
TOTAL (M&S = 500)	20,200
TOTAL (M&S = 832.7)	33,500

TABLE 8.12. FACTORED CAPITAL COST FOR CHROMIUM PHOSPHATE PRECIPITATION, SOLID/LIQUID SEPARATION

	Cost ($, M@S = 832.7)
1. Purchased Equipment Costs	33,500
2. Installed Equipment Costs (1.4 x Item 1)	46,900
3. Process Piping (30% of 2)	14,100
4. Instrumentation (10% of 2)	4,700
5. Auxiliaries (5% of 2)	2,400
6. Outside Lines (5% of 2)	2,400
7. Total Physical Plant Costs (Sum 2 through 6)	70,500
8. Engineering and Construction (20% of 7)	14,100
9. Contingencies (15% of 7)	10,600
10. Size Factor (Small Commercial, 10% of 7)	7,100
11. TOTAL PLANT FIXED CAPITAL COSTS	102,300
YEARLY COST, Based on 5 year pay-off period, 12% interest.	36,100

TABLE 8.13. CHROMIUM PHOSPHATE FUSION, CHROMATE LEACH, PHOSPHATE REMOVAL, S/L SEPARATION

	Cost, $ (M&S = 500)
Fusion	
1. Rotary Kiln Includes refractory lining, firing system, hot cyclone, water cooling, 6ft diameter, 8ft length $C = 140{,}000(2.5\text{tpd}/30\text{tpd})^{0.6}(500/540)$	28,900
Chromate Leach	
2. Leach Tank with agitator: $C = 27.5(340\text{gal})^{0.629}$	1,100
Phosphate Removal	
4. As in 2.	1,100
Solid/Liquid Separation	
5. Drum Filter: $C = 8235(16\text{ft}^2)^{0.292}$	18,500
6. Repulp Tank: $C = 27.5(100\text{gal})^{0.629}$ with agitator	500
TOTAL (M&S = 500)	50,100
TOTAL (M&S = 832.7)	83,400

TABLE 8.14. FACTORED CAPITAL COST FOR CHROMIUM PHOSPHATE FUSION, CHROMATE LEACH, PHOSPHATE REMOVAL, SOLID/LIQUID SEPARAION

		Cost ($, M@S = 832.7)
1.	Purchased Equipment Costs	83,400
2.	Installed Equipment Costs (1.4 x Item 1)	116,800
3.	Process Piping (30% of 2)	35,000
4.	Instrumentation (10% of 2)	11,700
5.	Auxiliaries (5% of 2)	5,800
6.	Outside Lines (5% of 2)	5,800
7.	Total Physical Plant Costs (Sum 2 through 6)	175,100
8.	Engineering and Construction (20% of 7)	35,000
9.	Contingencies (15% of 7)	26,300
10.	Size Factor (Small Commercial, 10% of 7)	17,500
11.	TOTAL PLANT FIXED CAPITAL COSTS	253,900
	YEARLY COST, Based on 5 year pay-off period, 12% interest.	89,500

TABLE 8.15. CHROMATE PURIFICATION, S/L SEPARATION, RELEACH, S/L SEPARATION

	Cost, $
	(M&S =500)
Purification	
1. Precipitation Tank: $C = 27.5(120\text{gal})^{0.629}$ with agitator	600
2. Solid/Liquid Separation	19,000
Releach	
3. Releach Tank: $C = 27.5(120\text{gal})^{0.629}$ with agitator	600
4. Solid/Liquid Separation	19,000
5. Storage Tank: $C = 0.897(1060)^{0.897}$, fiberglass	500
TOTAL (M&S = 500)	39,700
TOTAL (M&S = 832.7)	66,100

TABLE 8.16. FACTORED CAPITAL COST FOR CHROMATE PURIFICATION, SOLID/LIQUID SEPARATION, RELEACH, SOLID/LIQUID SEPARATION

		Cost ($, M@S = 832.7)
1.	Purchased Equipment Costs	66,100
2.	Installed Equipment Costs (1.4 x Item 1)	92,500
3.	Process Piping (30% of 2)	27,800
4.	Instrumentation (10% of 2)	9,300
5.	Auxiliaries (5% of 2)	4,600
6.	Outside Lines (5% of 2)	4,600
7.	Total Physical Plant Costs (Sum 2 through 6)	138,800
8.	Engineering and Construction (20% of 7)	27,800
9.	Contingencies (15% of 7)	20,800
10.	Size Factor (Small Commercial, 10% of 7)	13,900
11.	TOTAL PLANT FIXED CAPITAL COSTS	201,300
	YEARLY COST, Based on 5 year pay-off period, 12% interest.	71,000

TABLE 8.17. ZINC SOLVENT EXTRACTION, ZINC SULFATE CRYSTALLIZATION EQUIPMENT LIST AND FACTORED CAPITAL COST

Cost data are not available for commercial zinc solvent extraction facilities. The equipment required is, however, similar to that required for copper solvent extraction. The major difference is the number of cells. For copper solvent extraction the previous cost was based on three stages of extraction and two stages of stripping. The zinc-iron solvent extraction cost is estimated based on the following assumptions:

a. Solvent extraction of residual iron and zinc requires ten cells for loading/stripping. The capital cost/cell (based on Cu SX) is \$32,500. Therefore, for iron and zinc the FCC = 325,000.

b. Zinc sulfate crystallization is estimated: 500 gal/day of strip solution containing 132 gpl zinc. A batch crystallizer cost (24) is \$19,000 @ an M&S of 270. Therefore, the crystallizers present cost estimate is:

$$\text{Cost} = 19{,}000(832.7/270) = \$58{,}600$$

c. The hydrochloric acid strip solution generated per day is 330 gal containing 18 gpl iron. A small pilot size SX plant to recover the HCl would be required using Amberlite LA-2 (25). The volume of solution to be treated is very small (330 gal/d) compared to the volume of treated leach solution (22,300 gal/d). Two mixer-settlers would be required for extraction and two for stripping. The cost for four cells is estimated from Wood to be:

$$\text{Cost} = 7000\,(832.7/600)$$

$$= \$9{,}700/\text{cell}.$$ Total cost for four cells would be \$38,800. This includes mixer-settlers, explosion proof motor, drive, piping, concrete, steel, instruments, electrical, insulation, paint.

d. The concentrated ferric chloride may be a marketable product or may be used in the chromate purification unit operation but neither a credit nor a penality is taken for disposal.

The FCC total cost for solvent extraction, crystallization, and stripping of hydrochloric acid from the DEHPA strip solution is \$422,400. A one time cost for reagents is included in the capital cost, i.e., \$14,200. Therefore, the total FCC is 436,600

The operation cost is	148,900
The total annualized cost is	585,500

8.2.9. NICKEL SOLVENT EXTRACTION, ELECTROWINNING

The factored capital cost is presented in Table 8.18.

TABLE 8.18. NICKEL SOLVENT EXTRACTION, ELECTROWINNING FACTORED CAPITAL COST

Cost data are estimated from the Solvent Extraction Handbook (16): i.e., a nickel solvent extraction-electrowinning integrated system including heat exchange, flotation, electrowinning, and carbon adsorption has a cost estimate of $\$9.36\times10^6$ for a capacity of 12.5×10^{10} gm/yr at an M&S = 600.

The Factored Capital Cost for the present system is, therefore:

$$\text{F.C.C.} = 9.36\times10^6(4.82\times10^8/12.5\times10^{10})^{0.7}(832.7/600)$$

$$= \$265{,}400$$

F.C.A.C. = 93,500

Operating = 38,300

Total = 131,800